General paper

X-Ray Evaluation of Pulse-Plated Crack-Free Cr Layer

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Abstract: Several crack-free Cr plating processes using pulse-current electrolysis have been proposed for improving corrosion resistance. However, industrial applications of crack-free Cr platings are very few since these Cr layers are subjected to tensile residual stress and easily form macrocracks after plating operations, particularly at temperatures higher than 373K. The residual stress of crack-free Cr layers deposited by pulse-current electrolysis was evaluated by the X-ray diffraction method. With changing pulse conditions, various residual stresses were measured. The specimen in which initial compressive residual stress of the Cr layer exceeded -150MPa did not form macrocracks after holding at 473K for 2h, and showed a high corrosion resistance without rusting even after a 700h neutral salt spray test (NSST). The amount of change in the residual stress as a result of heat treatment correlated with the integral breadth of the diffraction profile, and became smaller and more stable with heat treatment as the integral breadth became narrower.

Key words: X-ray stress measurement, Pulse current electrolysis, Crack-free Cr layer, Residual stress, Integral breadth

1. INTRODUCTION

Since a hard Cr plating offers high corrosion and wear resistances and a small coefficient of friction, it has been used in various industries, including the automobile industry, in components such as piston rods used for shock absorbers, piston rings and cylinder liners, as well as in shafts of hydraulic equipment, rolls for printing and rolling, and metal molds [1,2]. Cr plating layers usually have fine cracks (hereafter, channel cracks), and the steel substrates rust due to the infiltration of corrosive liquids through the cracks. For this reason, corrosion resistance is influenced not only by the thickness of the plating layers but also by the width and the depth of the channel cracks [3]. It is well known that channel cracks can be filled and corrosion resistance improved by applying finishing processes such as buff polishing after plating [2].

Several methods have been proposed for improving corrosion resistance through the deposition of a Cr plating layer without channel cracks (hereafter, crack-free Cr plating) using pulse-current electrolysis [4,5]. However, industrial applications of crack-free Cr plating are very few since these plating layers are subjected to tensile residual stress and easily form macrocracks after plating operations [6], particularly at temperatures higher than 373K.

The reason for the formation of macrocracks in the plating layer is that plating layers shrink at high temperatures; the plating layer is thought to be influenced by residual stress and lattice defects. Considering such circumstances, if factors such as residual stress and lat-

tice defects in the plating layer are controlled by optimizing the pulse-plating conditions, there is a possibility that crack-free Cr plating with high corrosion resistance can be achieved.

In this study, residual stress was examined by the X-ray stress measurement method for Cr plating layers formed under various pulse-plating conditions.

2. PULSE-CURRENT ELECTROLYSIS

The rectangular pulse waveform which is used in the present study is shown in Fig.1. The period of the pulse T is defined as $T = t_{\text{on}} + t_{\text{off}}$, and t_{on}/T denotes the duty cycle. I_p is the peak value of the pulse-current density, and the frequency of the pulse current is denoted by $1/T$. t_{on} represents on time, and t_{off} represents off time [7].

$$T = t_{\text{on}} + t_{\text{off}}$$
$$\text{Frequency (Hz)} = 1/T$$
$$\text{Duty cycle (\%)} = t_{\text{on}}/T$$
$$I_p \text{ (A/dm}^2\text{): Peak current density}$$

Fig.1. Rectangular pulse waveform.

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3. RESIDUAL STRESS AND CORROSION RESISTANCE OF PULSE-PLATED Cr LAYER

3.1. Experimental Method

A steel rod with an external diameter of 12.5mm and length of 250mm (JIS S25C) was used. Tables 1 and 2 summarize the plating bath conditions and pulse conditions, respectively, used in the preparation of the specimens. A Cr plating layer 20 μ m thick was deposited on the specimen surface under the conditions of frequency of 1.7 to 5.0kHz and duty cycle of 33 to 67%, using a pulse power source, DPR 20-30/100 (Dynatronix Inc.). Figure 2 shows examples of the current and voltage waveforms (*on time/off time* = 0.5ms/0.5ms). Each specimen was heated at 423 to 523K for 2h, and the relationship between heat-treatment temperature and residual stress of the plating layer was evaluated by the X-ray stress measurement method. The surfaces of the plating layer before and after heat treatment were observed by scanning electron microscopy (SEM). Furthermore, the neutral salt spray test (NSST) was carried out for up to 700h for every specimen before and after heat treatment in order to evaluate the corrosion resistance of the specimens.

The X-ray stress measurement apparatus PSF-2M (Rigaku Co.) was used. Table 3 summarizes the conditions of X-ray stress measurement. The iso-inclination method of applying a parallel beam was used for the measurement of the optical system. Note that the peak position of the X-ray diffraction profile was determined by the full-width at half maximum (FWHM) midpoint method.

In the X-ray stress measurement method, the distance between the crystal lattice planes is determined by means of X-ray diffraction analysis, and the stress on the specimen surface is calculated using the strain determined from the measurement [8]. As shown in Fig. 3, in a plane which includes the direction of the surface stress σ_x (x-axis) measured at point O and the normal direction to the surface (z-axis) of the specimen, the

Table 1. Plating bath solutions and temperature.

CrO ₃ , g/L	246
SO ₄ , g/L	3.0
Catalyst (Organo-sulfonic acid), %	100
Bath temperature, K	333

Table 2. Pulse conditions.

	A	B	C	D	E	F	G
On time, ms	0.1	0.4	0.3	0.2	0.15	0.3	0.1
Off time, ms	0.1	0.2	0.2	0.2	0.2	0.3	0.2
Frequency, kHz	5.0	1.7	2.0	2.5	2.9	1.7	3.3
Duty cycle, %	50	67	60	50	43	50	33
Peak current density, A/dm ²	80	90	105	120	120	120	120

Table 3. Conditions of X-ray stress measurement.

X-ray optics	Parallel beam ψ -constant
Characteristic X-rays	Cr-K α
Wave length, nm	0.229100
Filter	V
Tube voltage, kV	30
Tube current, mA	8
Irradiated area, mm ²	28.3 ($\phi 6$)
Fixed time, s	2
Slit divergence angle, deg	Incident; 1, Receiving; 1
Diffraction plane, hkl	Cr {211}
Scan angle, deg	143<2 θ <165
Step width, deg	0.25
ψ -angle, deg	Approximately 19.5, 61.9
Peak position	Half value breadth method

Fig.2. Example of the pulse waveform (*on time/off time* = 0.5ms/0.5ms).

Fig.3. X-ray diffraction of crystals [8].

distortion in the OP direction (the angle between the z axis and OP is ψ) is designated as ε_ψ , and the corresponding X-ray diffraction angle as $2\theta_\psi$ (θ_ψ : Bragg angle). Assuming that the stress condition is approximated by plane stress, the surface stress σ_x is expressed as [8].

$$\sigma_x = \frac{E}{1+\nu} \cdot \frac{\partial(\varepsilon_\psi)}{\partial(\sin^2 \psi)}$$

$$= -\frac{E}{2(1+\nu)} \cdot \cot \theta_0 \cdot \frac{\partial(2\theta_\psi)}{\partial(\sin^2 \psi)} \cdot \frac{\pi}{180}, \quad [\text{MPa}]$$

where, E is Young's modulus (MPa), ν is the Poisson's ratio, and $2\theta_\psi$ is the diffraction angle (deg).

In the X-ray stress measurement method, the stress in the polycrystals without texture is the target of measurement, and in this case, diffraction profile are obtained for any ψ value. For example, a Cr plate with the chemical composition shown in Table 4 was prepared by vacuum dissolution. The specimen was heated in a furnace at 1273K for approximately 3h and then cooled gradually to room temperature for 16h. When X-ray diffraction is carried out on the $\{211\}$ plane of the specimen using the characteristic Cr-K α X-rays, the relationship between $\sin^2\psi$ and the diffraction angle $2\theta_\psi$ and the relationship

Table 4. Chemical compositions of Cr plate (mass %).

O	N	S	C	Fe	Si	Cr
0.330	0.004	0.006	0.002	0.008	0.001	99.6

Fig.4. Peak intensity and $2\theta_\psi$ - $\sin^2\psi$ diagram.

between $\sin^2\psi$ and the peak intensity are obtained, as plotted by open circles in Fig 4 [9].

On the other hand, the Cr plating layer has a texture in which the $\{111\}$ plane grows parallel to the plating layer. Therefore, when X-ray diffraction is carried out on the $\{211\}$ plane of the specimen using the characteristic Cr-K α X-rays, diffraction are obtained only at the angle ψ based on the crystallographic azimuthal relationship [10]. In other words, diffraction occurs only around $\psi = 19.5\text{deg}$ and 61.9deg , as shown in Fig.4, and it is not possible to obtain the relationship between $2\theta_\psi$ and $\sin^2\psi$ directly.

Shiraiwa and Sakamoto proposed a method of calculating stress using the gradient M of a straight line connecting two diffraction angles, $2\theta_\psi$, measured at two points, $\psi = 19.5\text{deg}$ and 61.9deg [11]. Since this method has been widely used for the analysis of Cr plating layers [12-14] and other materials with textures [15-17], we adopted it in this study. For quantitative evaluation of stress by the X-ray stress measurement method, the X-ray stress constant K , explained previously, must be known. Therefore, the X-ray stress constant was experimentally obtained using the following method [9]. First, approximately 3mm of a Cr plating layer was deposited on a steel substrate (thickness: 5mm) by DC electrolysis. Then the steel substrate was removed and the plating layer was cut into a $60 \times 12 \times 2 \text{ mm}^3$ specimen. Several loads of bending stress were applied to the specimen to obtain the $2\theta_\psi$ - $\sin^2\psi$ diagram shown in Fig.5. Using the relationship between the gradient M ($\partial 2\theta_\psi / \partial \sin^2\psi$) obtained from Fig.5 and stress σ , the X-ray stress constant $K = -247 \text{ MPa/deg}$ was obtained.

In order to evaluate the value of the stress constant and the X-ray stress measurement method, the residual stress obtained by the X-ray stress measurement method was compared with that obtained by the spiral contract meter method (JIS H8626), in which only the outer

Table 5. Plating bath solutions and conditions.

CrO ₃ , g/L	250
SO ₄ , g/L	3.5
Catalyst (Organo-sulfonic acid), %	100
Bath temperature, K	333
Current density (Direct current), A/dm ²	50

Fig.5. $2\theta_\psi$ - $\sin^2\psi$ diagram under various loads [9].

Fig. 6. Relationship between residual stress and plating thickness (direct current electrolysis) [9].

surface of a spiral sample was plated and residual stress (deposition stress) was measured using the spiral helix angle.

On Cu plates of $25 \times 25 \times 1 \text{ mm}^3$ (JIS C1100), plating layers 2, 5, 10, 15, 20 and $30 \mu\text{m}$ thick were deposited by DC electrolysis under the conditions summarized in Table 5. The residual stress in each of the above plating layers was measured by the X-ray stress measurement method. The residual stress obtained is shown in Fig. 6, along with the residual stress obtained by the spiral contract meter method. As shown in Fig. 6, we confirmed that the residual stresses obtained by the two methods are in good agreement [9].

3.2. Results and Discussion

Crack-free Cr plating layers with residual stress in the range of -337 to 36 MPa were obtained. The relationship between heating temperature and residual stress of the plating layer after heat treatment and the relationship between heating temperature and the change in residual stress due to heat treatment are shown in Figs. 7 and 8, respectively. Figure 9 shows SEM micrographs of the plating layer surface of typical specimens (specimens B, C, D and G) as deposited and after heat treatment. Table 4 summarizes the results of NSST. The following was clarified from Figs. 7 to 9 and Table 6.

(1) When the specimens with residual stress in the range of -61 to 36 MPa in the plating layer (specimens A, B and C) were held at 473 K for 2h, the residual stress became more tensile by approximately 250 MPa , resulting in the generation of macrocracks.

(2) When the specimen with compressive residual stress of -151 MPa in the plating layer (specimen D) was held at 473 K for 2h, the residual stress became more tensile by approximately 220 MPa , but no macrocracks were generated. The threshold of the residual stress above which macrocracks are generated in the specimens held at 473 K is approximately 80 MPa .

(3) Assume the threshold of macrocrack generation in a plating layer to be approximately 80 MPa . In the specimens in which no macrocracks were generated after heat treatment, rusting did not occur after the neutral salt spray test for 700h, indicating high corrosion resistance. On the other hand, in the specimens in which

Fig. 7. Change in residual stress in the Cr plating layers due to heat treatment.

Fig. 8. Change in residual stress due to heat treatment and heat treatment temperature.

macrocracks were generated after heat treatment, rusting occurred within a relatively short period of 24h or less after the initiation of neutral salt spray testing.

(4) Under certain pulse-plating conditions, a crack-free Cr layer with compressive stress higher than -300 MPa was obtained. For these specimens (specimens F and G), the residual stress of the plating layer was compressive after being held at 523 K for 2h. The change in residual stress due to heat treatment was less marked than that of other specimens.

Based on the above results, by making the residual stress in the plating layer sufficiently compressive in order to exceed the change in the residual stress towards tensile stress due to heat treatment, the generation of macrocracks in the plating layer can be suppressed and high corrosion resistance can be obtained.

The residual stress of the plating layer has been shown to change towards tensile stress due to heat treatment. It is considered that the change in residual stress is caused by the shrinkage of the plating layer, which is itself caused by the diffusion and disappearance of lattice defects (vacancies) in the plating layer. The reason for the small change in the residual stress due to heat treatment of the specimens (specimens F and G) when compressive residual stress is higher than -300 MPa may be that the crystallites in the plating layer of the specimens are larger than those of other specimens and that the total amount of grain boundaries including

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Fig.9. SEM micrographs of Cr plating surface of typical specimens (specimens B, C, D and G) as deposited and after heat treatment.

Table 6. Results of NSST before and after heat treatment.

Holding temp. (holding time)	No.	Residual stress, MPa	Rusting
As plated	A	36	Not observed (700h)
	B	25	
	C	-61	
	D	-151	
	E	-239	
	F	-304	
	G	-337	
423K (2h)	A	144	Observed (< 24h)
	B	168	
	C	86	
	D	-35	Not observed (700h)
	E	-103	
	F	-209	
	G	-223	
473K (2h)	A	273	Observed (< 24h)
	B	273	
	C	163	
	D	73	
	E	-7	Not observed (700h)
	F	-184	
	G	-209	
523K (2h)	A	311	Observed (< 24h)
	B	355	
	C	182	
	D	106	
	E	7	Not observed (700h)
	F	-158	
	G	-168	

many lattice defects (total amount of grain boundaries relative to the total volume of plating layer) is small. In the next section, we discuss the measured distribution of the diffraction X-ray breadth (integral breadth), which has a close relationship to the size of crystallites, to clarify the residual stress and integral breadth of the plating layers obtained by pulse-current electrolysis.

4. RESIDUAL STRESS AND INTEGRAL BREADTH OF PULSE-PLATED Cr LAYER

4.1. Experimental Method

Cu plates of $65 \times 85 \times 1 \text{ mm}^3$ (JIS C1100) were used as specimens. A $6\text{--}8\text{ }\mu\text{m}$ -thick Cr plating layer (plating area: 1 dm^2) was deposited on the specimen surface under the conditions of frequency of 0.4 to 1.7kHz and duty cycle of 43 to 83%, using a DP 20-150/200 pulse power source (Dynatronix Inc.). For comparison, DC electrolysis was also performed. The reasons for using a Cu plate as a substrate and setting the thickness of the plating at 6 to $8\text{ }\mu\text{m}$ were threefold: (1) to observe the penetration of characteristic Cr-K α X-rays over the entire plating layer (when diffraction is performed on the Cr {211} plane, the penetration depth at $\psi = 61.9^\circ$ is approximately $8\text{ }\mu\text{m}$), (2) to prevent the influence of X-rays diffracted from the substrate metal (when the substrate includes Fe, the peak diffraction X-ray profile of the Fe {211} plane is approximately 156.4° , is close to well with the value of the Cr{211} plane, approximately 153.1°), and (3) when measuring the integral breadth, to observe the penetration of characteristic Cr-K α X-rays over the entire plating layer (when diffraction is performed on the Cr{222} plane, the penetration depth at $\psi = 0^\circ$ is approximately $6\text{ }\mu\text{m}$).

Table 7. Plating bath solutions and conditions.

CrO ₃ , g/L	246
SO ₄ , g/L	3.0
Catalyst (Organo-sulfonic acid), %	100
Bath temperature, K	333
Peak current density, A/dm ²	120

Table 8. Conditions of X-ray diffraction.

X-ray method	Focusing beam
Characteristic X-rays	Cu-K α
Wave length, nm	0.15405620
Filter	None
Monochromator	Graphite {0002}
Tube voltage, kV	50
Tube current, mA	40
Irradiated area, mm ²	1 $\times$ 10
Fixed time, s	1
Diffraction plane, <i>hkl</i>	Cr {222}
Scan angle and step width, deg	125<2 θ <150, 0.2
ψ -angle, deg	0

Table 9. Conditions of X-ray diffraction.

X-ray optics	Focusing beam
Characteristic X-rays	Cu-K α
Wave length, nm	0.15405620
Filter	None
Monochromator	Graphite {0002}
Tube voltage, kV	40
Tube current, mA	40
Irradiated area, mm ²	1 $\times$ 10
Fixed time, s	1
Scan angle and step width, deg	30<2 θ <70, 0.04

Table 7 summarizes the compositions of the plating bath solutions and the plating bath conditions used in the preparation of the specimens. The residual stress and integral breadth of the Cr plating layers of the specimens were evaluated by X-ray diffraction analysis. The conditions adopted in the X-ray stress measurement were the same as those listed in Table 3. For the measurement of integral breadth, the X-ray diffractometer RINT 2200 (Rigaku Co.) was used. The conditions for X-ray diffraction are summarized in Table 8. And, all specimens were analyzed by X-ray diffraction using the X-ray diffractometer JDX 3531 (JEOL Ltd.). The conditions for X-ray diffraction are summarized in Table 9.

4.2. Results and Discussion

The results obtained for residual stress and the integral breadth of the plating layers formed under various pulse conditions are summarized in Table 10. Figures 10 and 11 show the relationship between integral breadth and residual stress and the relationship between integral breadth of the as-plated sample and the change

Table 10. Pulse conditions and results of measurement.

No	Timing, ms		Frequency, kHz	Duty, %	Stress, MPa	Integral breadth, deg
	on	off				
H	---	---	---	100	296	3.776
I	1.4	0.3	0.59	82	-37	2.764
J	1.0	0.3	0.77	77	-155	2.669
K	0.6	0.3	1.11	67	-272	2.394
L	0.4	0.3	1.43	57	-305	2.311
M	0.3	0.3	1.67	50	-313	2.335
N	2.0	0.4	0.42	83	180	2.869
O	1.6	0.4	0.50	80	46	2.728
P	1.2	0.4	0.63	75	-204	2.498
Q	0.8	0.4	0.83	67	-297	2.353
R	0.6	0.4	1.00	60	-323	2.162
S	0.5	0.4	1.11	56	-334	1.945
T	0.4	0.4	1.25	50	-272	1.770
U	0.3	0.4	1.43	43	30	1.435
V	1.6	0.5	0.48	76	-163	2.714
W	1.2	0.5	0.59	71	-301	2.425
X	0.9	0.5	0.71	64	-131	2.130
Y	0.6	0.5	0.91	55	53	1.423

Fig.10. Relationship between residual stress and integral breadth.

Fig.11. Relationship between change in residual stress due to heat treatment (473K, 2h) and integral breadth before heat treatment.

in residual stress due to heat treatment, respectively. Open circles in Fig. 10 (specimens U and Y) indicate that chrome hydroxide (CrH) coexists in the plating layer. The X-ray diffraction line profile measurements of specimen U are shown in Fig. 12.

4.2.1. Substrate and residual stress on the Cr layer

The pulse conditions for specimen F described in section 3 and those for specimen M described in this section are identical, however, the material and shape of the substrate metal (specimen F: S25C rod; specimen M: C1100 plate) and plating thickness (specimen F: 20 μ m; specimen M: 8 μ m) differ. The residual stresses on the plating layer for specimens F and M are -304MPa and -313MPa, respectively; the changes in residual stress towards tensile stress after heat treatment at 473K are also similar, being 146MPa and 136MPa, respectively. Based on the above results, it is considered that the influences of the material and shape of the substrate metal and plating thickness on the residual stress in the obtained plating layer are small.

4.2.2. Direct-current electrolysis

The residual stress of the plating layer of specimen H prepared by DC electrolysis (open square in Fig. 10) was tensile, and the integral breadth was the largest. Since Cr atoms were deposited continuously in DC electrolysis, crystals grew in many places on the surface. Therefore, one crystal came into contact with other crystals before the crystal grew to a large size. As a result, numerous fine crystals were formed. The grain boundary became an unconformity and lattice defects (vacancies) were generated along the grain boundary. During the deposition, the crystals grew three-dimensionally, and then, some vacancies remained without being filled by atoms. Since vacancies were formed in a place that should be filled by atoms, attractive force was induced between atoms, resulting in the generation of tensile residual stress in the plating layer.

4.2.3. Pulse-current electrolysis

The residual stress and integral breadth of the plating layer obtained by pulse-current electrolysis differ greatly depending on the pulse conditions, as shown by

Fig. 12. X-ray diffraction profile of mixed *hcp* deposits (specimen U: *on time/off time* = 0.3ms/0.4ms).

solid circles in Fig. 10. In the case of pulse-current electrolysis, the number of Cr atoms deposited by one pulse (one “*on time*”) is less than the number of atoms which can form one atomic layer (for example, one atom is deposited per approximately 2nm² with 1 ms of *on time*), and after the deposition of atoms, there is an *off time*. During the *off time*, the deposited atoms move actively over the surface, similar to the case of DC electrolysis, and form crystals with other atoms. Note that unlike the case of DC electrolysis, an *off time* exists in pulse-current electrolysis; therefore, the possibility of crystals coming into contact with other crystals is low and each crystal can grow to a large size. In addition, the atoms which cannot find a place to settle move around the surface until they reach lattice defects at the grain boundary and fill the vacancies. Even when the space between atoms in the unconformity lattice defect area is less than the diameter of one atom, since the energy associated with invading the space between atoms is lower than that associated with moving around the surface, the atoms invade the space between other atoms, inducing compressive residual stress. When the *off time* is short compared to the number of deposited Cr atoms per pulse (specimens I, N and O), new atoms are deposited before the first atoms can fill the vacancies; this is similar to the case of DC electrolysis. In this case, it is considered that tensile residual stress and low compressive residual stress are generated in the plating layer.

On the other hand, when the *off time* is long compared to the number of deposited Cr atoms per pulse (specimens U and Y), hexagonal closed-packed chrome hydroxide (CrH) coexists in the plating layer, according to the X-ray diffraction line profile shown in Fig. 12 [18]. The reason for this is considered to be as follows: since many hydrogen (H) atoms, generated by electrolysis, exist in a nascent state in the neighborhood of the plating surface, when the supply of Cr atoms is insufficient due to a long *off time*, the deposited Cr atoms react with the H atoms to produce CrH.

4.2.4. Thermal stability and integral breadth

As shown in Fig. 11, it was found that the change in residual stress towards tensile stress after heat treatment at 473K for 2h correlates with the change in the integral breadth; the narrower the integral breadth, the smaller the change in residual stress towards tensile stress. The integral breadth is determined by the size of the crystallite and the amount of microstrain [19]. If it is possible to ignore the influence of microstrain, the larger the crystallite size, the more thermally stable the plating layer. In this case, it is estimated that contraction of the plating layer due to heat treatment is suppressed since the total amount of grain boundaries (total amount of grain boundaries relative to total volume of plating layer) is small, and as a result, the number of lattice defects (vacancies) which frequently exist in a grain boundary is also small.

Scherrer assumed that there are no imperfect crystals and that the distribution of the X-ray diffraction profile is determined only by the crystallite size [20].

On the premise that the crystallite size is uniform, the following Scherrer's equation, in which the crystallite size is calculated using the integral breadth, is derived.

$$D_{hkl} = \frac{K \cdot \lambda}{\beta \cdot \cos \theta} ,$$

where, D is the crystallite size (nm), λ is the X-ray wavelength (nm), β is the integral breadth of diffraction (rad), θ is the Bragg's angle (deg) and K is the constant (1.05).

The crystallite size is calculated using Scherrer's equation and is found to be approximately 6nm in the plating layer obtained by DC electrolysis, approximately 7 to 8nm in the plating layer with tensile residual stress obtained by pulse-current electrolysis, approximately 9 to 16nm in the plating layer with compressive residual stress obtained by pulse-current electrolysis, and approximately 18nm in the plating layer with coexisting CrH. In the calculation of these values, the integral breadth corrected using the Cauchy function was employed. For the correction of the apparatus constant, the Si {533} peak value was used.

Based on the above discussions, it was concluded that thermally stable crack-free Cr can be obtained (1) by making the residual stress in the plating layer a compressive stress of -150MPa or greater through the control of the pulse conditions and (2) by keeping the diffraction X-ray integral breadth of the plating layer within a certain range (in this study, the integral breadth was approximately 2.5deg or less; in this range, CrH is not generated).

5. CONCLUSIONS

The residual stress and integral breadth of the Cr layer deposited by pulse-current electrolysis under various pulse conditions were evaluated by means of X-ray diffraction. We reached the following conclusions.

- (1) Compressive residual stress exceeding -300MPa was obtained by pulse current electrolysis under the conditions of *on time* = 0.3ms and *off time* = 0.3ms.
- (2) The residual stress of the Cr plating layer changed toward tensile stress following heat treatment, and macrocracks were formed in the Cr plating layer when the residual tensile stress exceeded 80MPa after heat treatment.
- (3) The specimens in which the initial residual compressive stress of the Cr plating layer exceeded -150MPa did not form macrocracks after heat treatment at 473K, and showed a high corrosion resistance without rusting after a 700h NSST.
- (4) Other than the specimens in which CrH coexists in

the layer, the amount of change in the residual stress due to heat treatment correlated with the integral breadth, and became smaller and more stable following heat treatment as the integral breadth became narrower.

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