EFFECT OF HEAT TREATMENT ON RESIDUAL STRESS PROFILES OF PULSE-PLATED CRACK-FREE Cr LAYER

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ABSTRACT

The residual stresses of crack-free Cr layers deposited on a steel substrate by pulse current electrolysis were evaluated by X-ray diffraction methods. Changing the pulse conditions, various residual stresses were measured. The residual stress of the Cr layer changed toward to tensile following heat treatment, and macro cracks were formed in the Cr layer when the residual stress exceeded 80MPa in the tension after heat treatment. The specimens in which the initial compressive residual stress of the Cr layer exceeded -200MPa did not form macro cracks after being held at 673K for 2h. The amount of change in the residual stress due to heat treatment correlated with the half value breadth of the diffracted X-rays, and became smaller and more stable with heat treatment as the half value breadth became narrower.

INTRODUCTION

Hard Cr plating offers high corrosion resistance, high wear resistance and a small coefficient of friction. Therefore, Cr plating has been widely used for engineering purposes. Specific applications include those in the piston rods of shock absorbers, piston rings and cylinder liners, as well as those in the shafts of hydraulic apparatuses, rolls for metal rolling and metallic molds [1,2]. However, 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 depth of the channel cracks [3]. Several methods have been proposed for improving corrosion resistance by depositing a Cr plating layer without channel cracks (hereafter, crack-free Cr plating) using pulse-current electrolysis [4,5]. However, there are few industrial applications of crack-free Cr plating since these plating layers are subjected to tensile residual stress and easily form macro cracks after plating operations [6], particularly at temperatures higher than 373K. Accordingly, we have attempted to produce a crack-free Cr plating layer that has high compressive residual stress and does not form macro cracks after plating operations or at high temperatures, by controlling pulse-plating conditions. In this study, residual stress was examined by the X-ray stress measurement method for Cr plating layers formed under various pulse-plating conditions.

PULSE-CURRENT ELECTROLYSIS

The rectangular pulse waveform used in the present study is shown in Fig.1. The period of pulse \( T \) is shown by \( T = t_{on} + t_{off} \), and \( t_{on}/T \) denotes the duty cycle. \( I_p \) is the peak value of pulse-current density, and the frequency of pulse-current is denoted by \( 1/T \). \( t_{on} \) represents \textit{on time}, and \( t_{off} \) represents \textit{off time}. 

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EXPERIMENTAL DETAILS

Specimens
Steel rods (S25C JIS) with an outer diameter of 12.5mm and a length of 250mm are used as substrates for plating. The plating bath solutions and the pulse-plating conditions are shown in Tables 1 and 2. DPR20-30/100 (manufactured by Dynatronix, Inc.) was used for the pulse power supply, and a Cr plating layer with a thickness of 20µm was deposited onto the substrate surface. For comparison, specimens deposited using direct-current electrolysis were also prepared. Each of the specimens was held at room temperature for 23064h (961 days). On the other hand, other specimens were cooled to room temperature after being held at 423K to 673K for 2h.

Table 1. Plating bath solutions and temperature.

<table>
<thead>
<tr>
<th></th>
<th>CrO₃, g/L</th>
<th>SO₄, g/L</th>
<th>Catalyst (Organo-sulfonic acid), %</th>
<th>Bath temperature, K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>246</td>
<td>3.0</td>
<td>100</td>
<td>333</td>
</tr>
</tbody>
</table>

Table 2. Pulse-plating conditions.

<table>
<thead>
<tr>
<th></th>
<th>ton, ms</th>
<th>toff, ms</th>
<th>1/T, kHz</th>
<th>ton/T, %</th>
<th>Ip, A/dm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.1</td>
<td>0.1</td>
<td>5.0</td>
<td>50</td>
<td>80</td>
</tr>
<tr>
<td>B</td>
<td>0.4</td>
<td>0.2</td>
<td>1.7</td>
<td>67</td>
<td>90</td>
</tr>
<tr>
<td>C</td>
<td>0.3</td>
<td>0.2</td>
<td>2.0</td>
<td>60</td>
<td>105</td>
</tr>
<tr>
<td>D</td>
<td>0.2</td>
<td>0.2</td>
<td>2.5</td>
<td>50</td>
<td>120</td>
</tr>
<tr>
<td>E</td>
<td>0.15</td>
<td>0.2</td>
<td>2.9</td>
<td>43</td>
<td>120</td>
</tr>
<tr>
<td>F</td>
<td>0.1</td>
<td>0.2</td>
<td>3.3</td>
<td>33</td>
<td>120</td>
</tr>
<tr>
<td>G</td>
<td>0.4</td>
<td>0.3</td>
<td>1.4</td>
<td>57</td>
<td>110</td>
</tr>
<tr>
<td>H</td>
<td>0.3</td>
<td>0.3</td>
<td>1.7</td>
<td>50</td>
<td>120</td>
</tr>
<tr>
<td>I</td>
<td>Direct-current electrolysis</td>
<td>100</td>
<td>60</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

X-Ray Analysis of Cr Plating Layer
A Cr plating layer exhibits a high {111} orientation. When the {111} plane of the cubic lattice lies parallel to the plating surface, the 211 diffraction appears at ψ₁ = 19.5 deg and ψ₂ = 61.9 deg [7-9]. This is illustrated by the 211 pole figure in Fig.2 covering a range of 0 deg < ψ < 70 deg. ψ is the angle between the normal of the lattice plane and the normal of the plating surface. X-ray stress measurement was performed with Cr-Kα radiation. For the specimen used in this study, the residual stress σ was derived in the 211 diffraction plane at 2θ = 153.15 deg, using Eq. (1),

\[
\sigma = K \cdot \frac{2\theta(\psi_1) - 2\theta(\psi_2)}{\sin^2 \psi_1 - \sin^2 \psi_2}
\]  

(1)
where \(2\theta\) and \(K\) are the diffraction angle evaluated by Bragg's law and the X-ray stress constant of the Cr plating layer, respectively. The value of \(K\) used in the present study is -247MPa/deg [10]. The residual stress of the plating layer of each specimen as-plated and after heat treatment was measured by the X-ray stress measurement method. The X-ray diffraction conditions are shown in Table 3. The half value breadth was measured at \(\psi = 19.5\text{deg}\).

Table 3. Conditions of X-ray stress measurement

<table>
<thead>
<tr>
<th>X-ray method</th>
<th>Parallel beam, (\psi)-constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Characteristic X-rays</td>
<td>Cr-Ka</td>
</tr>
<tr>
<td>Filter</td>
<td>V</td>
</tr>
<tr>
<td>Tube voltage</td>
<td>30kV</td>
</tr>
<tr>
<td>Tube current</td>
<td>8mA</td>
</tr>
<tr>
<td>Irradiated area</td>
<td>28.3mm(^2)</td>
</tr>
<tr>
<td>Fixed time</td>
<td>2s</td>
</tr>
<tr>
<td>Diffraction plane</td>
<td>Cr {211}</td>
</tr>
<tr>
<td>Scan angle</td>
<td>143deg &lt; (2\theta) &lt; 165deg</td>
</tr>
<tr>
<td>Step width</td>
<td>0.25deg</td>
</tr>
<tr>
<td>(\psi) angle</td>
<td>19.5, 61.9deg</td>
</tr>
<tr>
<td>Peak position</td>
<td>Half value breadth method</td>
</tr>
</tbody>
</table>

Fig.2. Typical 211 pole figure of Cr plating layer.

EXPERIMENTAL RESULTS AND DISCUSSION

Residual Stress and Half Value Breadth

Figure 3 shows the residual stress of Cr plating layers and the half value breadth. The half value breadth is mainly determined by the crystallite size. A narrow half value breadth indicates a large crystallite size. The Cr plating layer deposited by direct-current electrolysis corresponding to the open circle in Fig.3, has high tensile residual stress, and its half value breadth is the widest among those of all specimens used.

In the direct-current electrolysis, since Cr atoms were deposited continuously, crystals grew in many places on the surface. And one crystal came in 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. Atoms deposited one after another, and the crystals grew three-dimensionally, as a result, some vacan-

Fig.3. Residual stress and half value breadth
cies 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.

On the other hand, the solid circles in Fig.3 show the residual stress and the half value breadth under various pulse-plating conditions. Changing the pulse conditions, various residual stresses were measured. For example, compressive residual stress exceeding -300MPa was obtained under the condition of \( t_{on} = 0.1\text{ms} \) and \( t_{off} = 0.2\text{ms} \), and tensile residual stress under the condition of \( t_{on} = 0.4\text{ms} \) and \( t_{off} = 0.2\text{ms} \). Figure 4 shows the relationships between the residual stress, the half value breadth and the duty cycle \( (t_{on}/T) \) when they were compared in the same \( t_{off} \) period \( (t_{off} = 0.2\text{ms}, \text{B, C, D, E and F in Table 2}) \). From Fig.4, the residual stress and the half value breadth are seen to be influenced by the duty cycle. In other words, the residual stress becomes more compressive and the half value breadth becomes narrower as the duty cycle becomes smaller. In the pulse-current electrolysis, the number of Cr atoms deposited in an \( t_{on} \) was less than that required to form one atomic layer (one Cr atom in an area of about 2nm\(^2\) when the \( t_{on} \) was 1ms)[11], and an \( t_{off} \) existed after the atoms deposition. Most of the atoms deposited during the \( t_{on} \) period actively moved around the surface and gradually formed a crystal on the surface with other atoms. However, since the \( t_{off} \) existed, the probability of a crystal interacting with other crystals was low; as a result, the crystal grew larger. Some atoms that did not form a crystal moved randomly over the surface until they settled in one of the vacancies at the grain boundaries. We consider that, from the point of view of surface energy, atoms settle into boundary defects similar to ‘cutting in’ even if the defects are slightly narrow for one atom to enter since this is more stable than moving around the surface. In this case, we consider the possibility of the occurrence of compressive residual stress.

![Graphs showing residual stress vs. duty cycle and half value breadth vs. duty cycle.](image)

**Fig.4.** Relationships between residual stress, half value breadth and duty cycle \( (t_{off} = 0.2\text{ms}) \).

### Thermal Stability and Half Value Breadth

Figure 5 shows the residual stress after heat treatment at the holding temperature. The residual stress changes toward to tensile for each of the Cr plating layers as the holding temperature increases. It is considered that these changes originate from the shrinkage of the plating layers by the diffusion and disappearance of vacancies.

Figure 6 shows the amount of change in the stress following heat treatment (i.e., the residual stress after heat treatment minus the residual stress of as-plated specimens) and the half value breadth of as-plated specimens. From Fig.6, the amount of change in the residual stress value following heat treatment is observed to correlate with the half value breadth; the amount becomes smaller as the half value breadth becomes narrower. A narrow half value breadth indicates a large crystallite size. From the result shown in Fig.6, it can be said that the larger the size of a crystal-
lite the more thermally stable it is. When the Cr plating layer has large crystallites, the grain boundaries are few, and the number of vacancies existing along the grain boundaries also decreases. In the present study, this is considered to have inhibited the shrinkage of the Cr plating layer by heat treatment.

**Residual Stress and Macro Cracks after Heat Treatment**

The solid circles in Fig.5 correspond to the occurrence of macro cracks. It can be understood that the threshold that determines whether macro cracks will occur or not is about 80MPa in tension after heat treatment. This is because the tensile strength of these Cr plating layers is approximately 80MPa. The specimens in which the initial residual stress of the Cr plating layer exceeded -200MPa in compression (E, G, H, and F) did not form macro cracks after heat treatment at 673K for 2h, and the specimens had high thermal stability.

**Change in Residual Stress at Room Temperature**

Figure 7 shows the relationship between the residual stress of the Cr plating layer and the holding time at room temperature. The residual stress changes toward to tensile for each of the Cr plating layers as the holding time increases. It is considered that these changes originate from the shrinkage of the Cr plating layers at room temperature.

Figure 8 shows the amount of change in the stress due to holding at room temperature for
23064h(961days) and the half value breadth of as-plated specimens. From Fig.8, the amount of change in the residual stress value due to holding at room temperature is observed to correlate with the half value breadth; the amount becomes smaller as the half value breadth becomes narrower.

The specimens A and B in which the initial residual stress was tensile formed macro cracks after being held for 1440h(60days). In contrast, the specimens F, G and H in which the initial residual stress was highly compressive did not form macro cracks after being held for 23064h(961days) and these specimens exhibit a residual stress change of approximately 50MPa toward the tensile side. It could be considered that macro cracks did not form in these specimens even when further expanding the holding time.

CONCLUSIONS

The conclusions drawn from examination of the pulse current electrolysis under various conditions, and evaluations of the resulting residual stress and the half value breadth of the Cr plating layer by X-ray diffraction methods, are as follows.

1. Compressive residual stress exceeding -300MPa was obtained by pulse current electrolysis under the conditions of on time = 0.1ms and off time = 0.2ms.
2. The residual stress and the half value breadth were influenced by the duty cycle when they were compared in the same off time period.
3. The residual stress of the Cr plating layer changed toward to tensile following heat treatment (or being held at room temperature), and when the residual stress exceeds 80MPa in tension after heat treatment (or being held at room temperature).
4. The amount of change in the residual stress due to heat treatment (or being held at room temperature) correlated with the half value breadth, and became smaller and more stable following heat treatment (or being held at room temperature) as the half value breadth became narrower.

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REFERENCES