THE MECHANISM OF THE NUCLEATION OF CORROSION CRACKS

K. N. Tseikovich and V. V. Gerasimov


UDC 620.194.2

X-ray diffraction analysis was used to study changes in the distribution of stresses of the first and the second kind in surface layers of stressed Cr18Ni10Ti steel specimens during the nucleation and growth of corrosion cracks. Based on the results obtained, a mechanism of nucleation of corrosion cracks in 18-8-type steels was postulated.

Despite the very large number of experimental and theoretical studies of the nucleation of corrosion cracks, the mechanism for this phenomena has not yet been elucidated. This is because of its complex nature and its dependence on a large number of factors; this is responsible for the fact that, depending on the approach used, studies of this problem give different, sometimes contradictory, results.

This article describes the results of an X-ray diffraction study of the redistribution of stresses of the 1-st and 2-nd kind and structural changes that take place in the surface layers of 18-8-type stainless steel during the nucleation and growth of corrosion cracks.

The experimental work was carried out on Cr18Ni10Ti steel ring specimens (as supplied) measuring 30 x 3 x 6 mm. The rings were made on a lathe. The specimen end faces plastically deformed during machining were electrolytically etched to remove the work-hardened material. Carefully degreased (in acetone) rings were held for different periods in a boiling aqueous solution containing 42% MgCl₂ + 5% FeCl₃ (at 154° C) after which they were used for X-ray diffraction measurements; at the same time, the depth of penetration of corrosion cracks was measured by a previously described [1] method.

Stresses of the 1-st and 2-nd kind were determined by X-ray diffraction measurements in a URS-501 camera with ionization recording. A BSV3 X-ray tube with an iron anode was used as the radiation source. The wavelength employed was KCo₁ = 1.93597 Å. Stresses of the 1-st kind were estimated from the displacement of lines (311) in relation to the time of exposure of specimens to the action of the corrosive medium; stresses of the 2-nd kind were estimated by measuring the half-width of these lines. Diffraction lines were recorded by marking intensities with the aid of a mechanical counter. The distance between points near the maximum of a diffraction line was 1'.

To determine the magnitude of stresses of the 1-st kind, the specimens held in a boiling solution of 42% MgCl₂ + 5% FeCl₃ were carefully washed in water and acetone and then mounted in a special device (Fig. 1) for X-ray diffraction analysis.

Fig. 1. Device for X-ray diffraction analysis of the surface of Cr18Ni10Ti steel ring specimens in a URS-501 camera.

Metallographic examination of Cr18Ni10Ti steel ring specimens held in a boiling solution of 42% MgCl₂ + 5% FeCl₃ showed that crack nucleation takes place on the generatrix of their outer cylindrical faces. In view of this,
bearing in mind that the cracks propagated in a direction normal to the outer specimen surface, one may conclude that
tensile stresses oriented along a tangent to the ring surface normal to the cylinder generatrix are present in the
specimen surface layers. It may, therefore, be assumed that the surface of a ring specimen of Cr18Ni10Ti steel is in
uniaxial tension; in all the calculations carried out below, this fact was taken into account.

Stresses of the 1-st kind in the specimen surface layers were calculated [2] from the formula

$$\sigma = \frac{E}{\mu} \cdot \frac{\Delta \theta}{\sin \theta},$$

where $\sigma$ is the unknown stress; $E$ is Young's modulus ($2 \cdot 10^4 \text{ kg/m}^2$); $\mu$ is Poisson's ratio equal to about 0.28; $\theta$ is the
Bragg angle; $\Delta \theta$ is the displacement of the maximum of a diffraction line from the position corresponding to the
stress-free state.

The value for the stress-free state was calculated starting from the Wulff-Bragg equation

$$n \lambda = 2d \sin \theta,$$

where $n$ is the sequence of reflection, $\lambda$ is the X-ray radiation wavelength, and $d$ is the interplanar spacing.

In our case, for lines (311), we have $d = 1.081 \text{ Å}$ [3], $n = 1$, and $\lambda = \lambda K_{\alpha 1} = 1.93597 \text{ Å}$; hence, $\sin \theta = 0.8954$
and $\theta = 63^\circ 34'$. For the determination of stresses of the 2-nd kind by X-ray diffraction the specimens were etched in an aqueous
solution containing 5% $\text{HNO}_3 + 5\%\text{H}_2\text{SO}_4 + 5\text{ mg/l}\text{ChM}$ (a corrosion inhibitor) at 90-100 °C for 40-60 min to remove the
corrosion products. Preliminary tests showed that such an etching treatment produces no changes in the stressed
state of the specimen surface layers and ensures complete removal of the corrosion products, while the addition of
corrosion inhibitor ChM promotes the passivation of the $\alpha$-phase on the surface of Cr18Ni10Ti steel and so makes it
possible to obtain data on the behavior of this phase in tests in chloride solutions. The presence of the $\alpha$-phase on
the surface of austenitic Cr18Ni10Ti steel was established, by X-ray diffraction, with the presence of the most intense
lines (110).

The results of X-ray diffraction measurements on Cr18Ni10Ti steel ring specimens previously held in a boiling
solution of 42% $\text{MgCl}_2 + 5\% \text{FeCl}_3$ are reproduced in Tables 1 and 2 and Fig. 2.

<table>
<thead>
<tr>
<th>Immersion time, hr</th>
<th>Wulff-Bragg diffraction angle</th>
<th>Displacement of lines (311) in relation to the stress-free state</th>
<th>Stresses of the 1-st kind, kg/mm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>63°21'</td>
<td>13'</td>
<td>21</td>
</tr>
<tr>
<td>0.5</td>
<td>63°28'</td>
<td>6'</td>
<td>19</td>
</tr>
<tr>
<td>1.5</td>
<td>63°27'</td>
<td>7'</td>
<td>12.5</td>
</tr>
<tr>
<td>2.5</td>
<td>63°24'</td>
<td>9'</td>
<td>16.5</td>
</tr>
<tr>
<td>3</td>
<td>63°26'</td>
<td>8'</td>
<td>13</td>
</tr>
<tr>
<td>12</td>
<td>63°28'</td>
<td>6'</td>
<td>10</td>
</tr>
</tbody>
</table>

The curve illustrating the redistribution of stresses of the 1-st kind during the propagation of corrosion cracks
has three clearly defined ranges. The first range (up to 0.5 hr) is characterized by a displacement of lines (311)
toward larger angles ($63°21' \rightarrow 63°28'$) which corresponds to a reduction in tensile stresses from 21 to 10 kg/mm².
The second range (0.5–2 hr) corresponds to a shift of the diffraction lines toward smaller angles ($63°28' \rightarrow 63°24'$)
and an increase in tensile stresses from 10 to 16.5 kg/mm². Finally, in the third range, there is a continuous shift of
lines (311) toward larger angles and a decrease in stresses of the 1-st kind. Comparison of curves illustrating the
variation in stresses of the 1-st kind and the propagation of corrosion cracks leads to a conclusion that the minimum
on the curves of the stresses of the first kind corresponds to the onset of the propagation of corrosion cracks, i.e.,
to the incubation period.

Data in Table 2 and Fig. 2 show stresses of the 2-nd kind after immersion in a boiling solution of 42% $\text{MgCl}_2 +
+ 5\% \text{FeCl}_3$ are sharply decreased; this decrease takes place during the first 0.5 hr, i.e., during the incubation period,