Electrochemical Characteristics of the Anodized Titanium Oxide Films in Sulfuric Acid

Branka Pešovski¹, Vesna Krstić², Silvana Dimitrijević²

¹ Mining and Metallurgy Institute Bor, Zeleni Bulevar 35, 19210 Bor, Serbia
² University of Belgrade, Technical Faculty in Bor, VJ 12, 19210 Bor, Serbia

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This article presents some research into titanium electrode anodizing in H₂SO₄ solutions in the potential range –1 to 5 V at different scan rates (10, 50, 100 mV s⁻¹) using cyclic voltammetry measurements. Linear potentiodynamic measurements had used before and after the oxide layer formed on the titanium surface. The characterization and the exact determination of the titanium oxides species on the Ti substrate surface had performed by XRD and SEM-EDS analyses. Three characteristic oxide peaks appeared in the electrochemical measurements. These had observed at 0.2 V, 2.3 V, and 3.5 V on cyclic voltammetry curves at all scan rates for all H₂SO₄ concentrations. Even more, cyclic voltammetry measurements showed that all peaks observed were evident even at higher scan rates. That suggested that robust oxidation of the Ti surface had occurred. Voltammetric tests showed that the passivation of the titanium surface was effective. XRD and SEM-EDS measurements confirmed the existence of TiO₂ species in a crystalline form on the titanium surface after anodizing in 3M H₂SO₄ and annealing the anodized Ti electrode at 400 °C in the airflow. A significant increase in the loading of TiO₂ film annealed at 400 °C of the previous anodized Ti anode in H₂SO₄ was registered.

1. INTRODUCTION

The exact nature of formed protective oxide films on the titanium surface during the anodization process is still not well known, even though, in the study of surface modifications, many of the latest techniques for the investigating of properties of such films have been used.¹⁻⁹ For oxide films formed at high voltages (>50 V), the existence of both crystal phases rutile, and anatase is evidence. For the formed films on the lower-voltage (<10 V) there are more uncertainties in interpretations of one or more of three natural crystal modifications of oxides (rutile, anatase, and brucite). Therefore, a series of different oxides of low-valent titanium is present in the oxide film.¹⁰⁻¹⁴ The thin anode films on titanium surfaces, predominantly amorphous structure have been found in the oxide film.¹⁵ In the oxide film: TiO₂, Ti₅O₉, and Ti₃O₅ oxides can be present depending on whether the oxidation process is carried out chemically (in the airflow in H₂SO₄, HCl, HNO₃, or NaCl solutions) or electrochemically (anode polarization at low or high potentials). Energy-dispersive X-ray spectroscopy (EDX) or transmission electron microscopy (TEM) of the anodized oxide films has shown that the nature of TiO₂ film is also amorphous. Therefore, the presence of the anatase crystals depends on the anode potential.¹⁶,¹⁷ The disagreements related to the morphology, increase in thickness, and crystallographic structure of the surface titanium oxides can result from differences in the surface preparation, type of solvent, methods of preparation, and conditions of growth of crystals.¹⁸⁻²² Literature data show the dependence of oxide film structure on the rate of film thickness growth. It has also suggested that the degree of solubility of films increases significantly with a slight increase in the oxide film thickness.²³ It has also been shown that the films formed at a scan rate of 1 mV⁻¹ dissolve almost ten times more slowly than those at 1 V⁻¹. The most likely explanation for this effect is that the aging of slowly growing films leads to a denser crystalline structure with an accompanying increase in a barrier height for ions migration. Electrochemical dissolution of the passive film occurs at the boundary of the oxide-solution phase, according to equation (1), where the dissolution is not localized.²⁴

\[ TiO_2 + 3H^+ + e^- \rightarrow Ti(OH)^{2+} + H_2O \] (1)

The electrochemical parameters significantly influence the behavior and characteristics of titanium oxide growth. The growth of the oxide film thickness results in systematic changes in surface topography, especially in the pore surface configuration. Anionic incorporation into the oxide film will not change the chemical composition, crystals type, or the titanium oxide structure such as anatase, rutile, and even rare brucite.²⁵,²⁶ According to many researchers, a constant increase in the anode film thickness is a variable value because it changes over time.²⁷,²⁸ It significantly affects the surface properties of anodic oxide films and the forming of an intermediate layer of the TiO₂-x suboxide between a deep TiO layer of titanium substrate and a higher surface TiO₂ layer.²⁹ The structure of anode film changes from the amorphous to the crystalline phase, which forms above the “critical” thickness of oxide film. Changes in the electrochemical parameters have quantitative and qualitative effects on electrochemical behavior. These changes also increase the current efficiency and the growth rate of the formed titanium oxide films. Of
Anodizing titanium in sulfuric acid solutions has been extensively studied due to its potential applications in various fields, such as coatings for medical devices and as a functional surface modification for mechanical components. The formation of titanium oxide layers in sulfuric acid solutions is a complex process influenced by several factors, including the type of acid, concentration, temperature, and potential applied during the anodization process. The resulting oxide layers can exhibit a range of properties, from amorphous to polycrystalline, which depend on the parameters of the anodizing process.

### Chemical Reactions

Several chemical reactions occur during the anodization of titanium in sulfuric acid solutions. The main reactions involved are:

1. **Formation of Monoxide Layer:**
   
   \[ TiO_2 + 4H^+ \rightarrow Ti^{4+} + 2H_2O \]  

2. **Oxidation of Titanium:**
   
   \[ Ti + 3H^+ \rightarrow Ti^{3+} + 3H_{ads} \]  

In aerated solutions, titanium(IV) ions are oxidized according to the following reaction:

\[ 2H^+ + 2Ti^{3+} + 1/2 O_2 \rightarrow 2Ti^{4+} + H_2O \]  

### Experimental Characterization

The electrochemical characteristics of the anodized titanium oxide films in sulfuric acid have been extensively investigated. These studies involve the measurement of polarization curves, cyclic voltammetry, and potentiodynamic experiments to understand the electrochemical behavior of the oxide layers. The electrochemical procedures include the use of a three-electrode cell with a titanium electrode as the working electrode, Pt as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. The temperature is maintained at 25°C throughout the experiments.

### Structural Characterization

The structure of the oxide films is characterized using X-ray diffraction (XRD) to identify the phases present in the oxide layers. The diffraction patterns are compared with the International Centre for Diffraction Data (ICDD) standard data. The XRD analysis is performed using a Rigaku MiniFlex 600 with a D/teX Ultra 250 high-speed detector and copper anode X-ray tube. The anodized samples are coated with a thin layer of platinum for a better signal detection.

### Conclusion

The electrochemical characteristics of the anodized titanium oxide films in sulfuric acid solutions have been thoroughly investigated. The results provide a detailed understanding of the oxide layer formation, electrochemical behavior, and structural properties, which are essential for the development of new applications. Further studies are needed to optimize the anodization process and to explore the potential of these oxide films in various fields.
The surface appearance and mineralogical composition investigation of the samples SEM (JEOL, JSM IT 300LV) and EDS (OXFORD Instruments) analyses were applied.

2.1 Materials and solutions

The working electrode was made of a titanium plate, like a spatula shape in the lower part, and dimensions of 1.5 × 1.5 × 2.0 cm, with a handle-length of 15.0 cm. Grade II indicates the degree of titanium purity with a chemical composition shown in Table 1.

Table 1. The degree of Grade II titanium commercial purity.

<table>
<thead>
<tr>
<th>Content</th>
<th>Purity degree Grade II (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N (max.)</td>
<td>0.03</td>
</tr>
<tr>
<td>C (max.)</td>
<td>0.10</td>
</tr>
<tr>
<td>H (max.)</td>
<td>0.0125</td>
</tr>
<tr>
<td>Fe (max.)</td>
<td>0.30</td>
</tr>
<tr>
<td>O (max.)</td>
<td>0.25</td>
</tr>
<tr>
<td>Ti</td>
<td>The rest</td>
</tr>
</tbody>
</table>

The working solution was sulphuric acid, 96 % H₂SO₄ p.a. quality, manufactured at the “Zorka Factory” in Šabac, Serbia.

3. RESULTS & DISCUSSION

3.1 Cyclic Voltammetry

Figure 1. shows, respectively, the CV curves recorded in sulphuric acid solutions of different concentrations at different scan rates in the potentials range of –1.0 to 5.0 V. All processes essential for the investigation of this system are in the selected potential range.

The way that section titles and other headings are displayed in these instructions, is meant to be followed in your paper. An important parameter is the change in the scan rate because it influences the surface oxidation of the Ti-anode. The occurrence of the characteristic peaks that define the specific oxides assigned for the given test parameters was also supervised. The three apparent peaks at potentials 0.2, 2.2, and 3.5 V vs. SCE had detected at all scan rates. These current peaks formation are limited by the diffusion-controlled process.

Based on the CV curves shown, it is evident that after the titanium region presented in the active state, titanium oxidation took place, and the growth of the oxide film was usually in the form of TiO₂ structure. It is suggested in recent data in literature that the first peak in the cycle may occur due to the formation of the titanium oxides with the lower Ti-valence. These would probably be Ti²⁺ and Ti³⁺ in the form of TiO and Ti₂O₃ oxides, while the second and the third peaks correspond to the forming of TiO₂ films. Moreover, the layer that is formed mostly of TiO₂ oxide was seen to have protective characteristics. The oxidation of a titanium substrate is shown by the following equation:

\[ Ti + 2H₂O → TiO₂ + 4H^+ + 4e^- \]  \hspace{1cm} (6)

In addition to TiO₂, Ti₃O₅ also can be formed as an unstable compound. Therefore Ti₃O₅ oxide was rapidly oxidized to TiO₂ in contact with water according to the reaction:

\[ Ti₃O₅ + H₂O → 2TiO₂ + 2H^+ + 2e^- \]  \hspace{1cm} (7)

In all concentrations of sulphuric acid solutions tested at higher scan rates, the intensity of current peaks increases and indicates forceful titanium oxidation, which causes difficulty of a stable and compact film formation on the titanium surface. Blackwood et al. also showed that the stability of a potentiodynamic formed oxide film depends on the scan rate.

\[ 10 \text{ mV s}^{-1} \]
\[ 50 \text{ mV s}^{-1} \]
\[ 100 \text{ mV s}^{-1} \]

Figure 1. Titanim cyclic voltammograms in: A) 1.5 M, B) 1.0 M, C) 0.5 M of H₂SO₄ solution, respectively. The scan rate: 10, 50 and 100 mV s⁻¹.
Moreover, an increase in the intensity of current peaks in the concentration range examined indicates the diffusion-controlled process. 40

The so-called “low-voltage oxide films” characteristic of voltages below 20 V (usually up to 5 V) can have an amorphous structure and defective stoichiometry, while crystalline TiO2 occurs at higher potentials. 38,42 The intermediate TiO and TiO2-x layers are inserted between the TiO layer on the titanium surface and the outer TiO2 oxide layer, which is why the composition of such films is not uniform. 20,11 Besides, the composition of electrolytes also has a strong influence on the crystallinity of formed TiO2. 43 Furthermore, the crystalline TiO2 with a compact structure arises in the electrolyte with a higher water amount. 42 Nevertheless, the mechanism of the formation of the crystalline oxide form is still unclear. Probably solution impurities affect the conversion of formed amorphous film to the crystalline type in the coating. 44 The most common type of crystalline TiO2 is in the form of anatase in the anodization. The anatase type of TiO2 oxide gives a characteristic yellow color to the oxide film, 27 obtained in our experiments. The disagreement in the literature data may be due to the different surface preparation and the conditions in which the growth of the oxide occurred, shown by the instant current density, chemical composition (solution concentration), and electrolyte temperature. 4

Furthermore, according to curves presented in Figure 1, the current density increases at all recording speeds at the potentials above 2 V, probably due to the start of intense oxygen evolution and the formation of unstable titanium peroxide TiO2.

Moreover, the sharp decrease in the current density in the reverse scan is because of the passivation with an oxide film, consisting of oxides formed on the titanium surface. The stoichiometry of these oxides had not entirely determined in experimental studies, but the following oxides: TiO, TiO2, Ti2O3, 30,45,46,47 and the most stable TiO2 oxide most probably formed. The current peak at a potential around –0.23 V vs. SCE indicates, as well, a reduction of the unstable species on the metal surface. 32 Nevertheless, in the sulphuric acid solutions, Ti4+ ions are relatively facilely reduced to Ti3+ and Ti2+ species.

Figure 2. shows the CV curves obtained in sulphuric acid solutions. It can seem that an increase in the number of cycles leads to a significant decrease in the current density and the disappearance of the current peaks. That was easy to spot in the first cycle when the titanium oxide layers covered the surface. These layers had a significant variation in their stoichiometry and morphology, indicating oxidation of the unstable TiO and TiO2 type oxide species, like TiO, and Ti2O3, on the metal surface. It is also noticeable that after the first cycle at all concentrations of H2SO4, complete passivation of the titanium surface with stable TiO2 occurred.

3.2 Open circuit potential

Open circuit measurements of Ti and (Ti+TiO2)-electrodes had performed for 60 min in different concentrations of sulphuric acid solutions and the results obtained are presented in Figure 3, and Table 2. Based on the curves shown in Figure 3, it can see that in the sulphuric acid solutions, immediately after the electrode immersion, there is a sudden drop in the value of the open circuit potential, which most likely indicates titanium oxide dissolution on the electrode surface. Blackwood et al. found that the oxide film dissolution rate was the first-order reaction, given the proton concentration, and proposed the following dissolution reaction in an acidic solution. 33

On the OCP values of the potential for the (Ti+TiO2)-electrode at t=3600 s in 1.5 M and 1 M H2SO4, the formation of the oxide film occurs at more positive potentials in comparison to other H2SO4 concentrations. On the OCP potential for the Ti-electrode at t=3600 s in the same H2SO4 concentrations, the oxide film formation occurs at more negative potentials in comparison to 0.1 M and 0.05 M H2SO4 concentrations.

A deviation in the OCP potential value in 0.5 M H2SO4 at t=3600 s is observed. The oxide film formation on Ti-electrode occurs at a more positive potential, and on the (Ti+TiO2)-electrode occurs at a more negative potential value in comparison to all other H2SO4 concentrations.
Figure 2. Titanium cyclic voltammograms in different 
H₂SO₄ concentrations: A) 1.5 M, B) 1.0 M, C) 0.5 M, D) 0.1 
M, E) 0.05 M. The scan rate is 50 mV s⁻¹.

\[ TiO_2 + H_2O + H^+ \rightleftharpoons Ti(OH)_4^+ \]  \hspace{1cm} (8)

However, the value of the open circuit potential (OCP) 
increases by the further increase in anodization time that is a 
consequence of the thicker layer formation of oxide films on 
the titanium surface.\textsuperscript{19,35}

Table 2. The potential values for a Ti-electrode on OCP in 
different H₂SO₄ concentrations.

<table>
<thead>
<tr>
<th>Potential on r = 3600 s</th>
<th>H₂SO₄ concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>E / V\textsubscript{SCE}</td>
<td>1.5 M</td>
</tr>
<tr>
<td>–0.0636</td>
<td>–0.0926</td>
</tr>
</tbody>
</table>

Based on data in Table 2., and Figure 3. it can conclude 
that because of the change in the H₂SO₄ concentration, in 
general, no significant deviation occurs in the oxidation 
process and formation of the oxide film on the electrode 
surface, both for bare Ti-electrode, as well as for (Ti+TiO₂)- 
electrode.

Figure 3. The plot of the open circuit potential of (Ti+TiO₂)- 
electrode in different concentrations of H₂SO₄ solutions.

3.3 Linear potentiodynamic measurements

Figure 4. shows polarization curves in the various 
concentrations of sulphuric acid solutions of the titanium 
electrode and (Ti+TiO₂)-electrode. A rapid formation of the 
oxide film observes from the polarization curves of the anode 
process at the beginning of the polarization process. By the 
further anodization process the passivation of the titanium 
surface causes increases in the potential because of the growth 
and the alignment of the oxide layers surface.\textsuperscript{48}

In the furthest course of the oxidation process, on potentials 
higher than 1.5 V, there is an increase in the current density 
that undoubtedly indicates further oxidation of titanium. The 
passivation in the whole range of concentration observes. In 
the concentration range from 0.05 M to 0.5 M, a passivation 
plateau starts at the potential of 0.4 V vs. SCE. With a further 
increase in the concentration, the beginning of the passivation 
plateau moves to lower potential values: 0.345 V vs. SCE in 1 
M H₂SO₄ and 0.3 V vs. SCE in 1.5 M H₂SO₄. Moreover, the 
current density is constant in a wide range of potentials and 
increases at 1.54 V vs. SCE in 0.05 M H₂SO₄ up to 1.65 V vs. 
SCE in 1 M H₂SO₄ and 1.5 M H₂SO₄, suggesting that titanium

oxides formed are more stable in a solution of a higher sulphuric acid concentration. However, the current density increases at those potentials are due to the film dissolution on the titanium surface. The polarization curves of treated titanium electrodes indicate a lesser metals dissolution. In the pretreatment processes of titanium in H₂SO₄ solutions, the formation of a thicker oxide film on the titanium surface causes the lower current density anodization values. Furthermore, cathodic polarization curves detect a reduction of unstable titanium oxides with low-valence titanium, which has a good agreement with cyclic polarization measurements.

Based on the polarization curves presented in Figure 4, have determined kinetic parameters of electrochemical processes in the mediums investigated: the corrosion potential (E_corr), corrosion current density (i_corr), anodic (b_a), and cathodic (b_c) Tafel's slopes, which have presented in Table 3.

Table 3. Electrochemical parameters of (Ti+TiO₂)-electrode

<table>
<thead>
<tr>
<th>H₂SO₄ concentration</th>
<th>E_corr /mV</th>
<th>i_corr /mA cm⁻²</th>
<th>b_a</th>
<th>b_c</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5 M</td>
<td>-0.44 · 10⁻²</td>
<td>1.74 · 10⁻⁴</td>
<td>545.26</td>
<td>-283.53</td>
</tr>
<tr>
<td>1 M</td>
<td>7.84 · 10⁻²</td>
<td>1.57 · 10⁻⁴</td>
<td>359.59</td>
<td>-106.90</td>
</tr>
<tr>
<td>0.5 M</td>
<td>-8.86 · 10⁻²</td>
<td>1.18 · 10⁻⁴</td>
<td>597.20</td>
<td>-332.40</td>
</tr>
<tr>
<td>0.1 M</td>
<td>-1.44 · 10⁻²</td>
<td>3.29 · 10⁻⁵</td>
<td>111.98</td>
<td>-671.43</td>
</tr>
<tr>
<td>0.05 M</td>
<td>-7.32 · 10⁻²</td>
<td>2.70 · 10⁻⁵</td>
<td>357.21</td>
<td>-428.33</td>
</tr>
</tbody>
</table>

Table 4 also shows the coverage degree of the titanium surface at different concentrations of H₂SO₄ at the potentials 0.5 V, 1.0 V, and 1.5 V, to obtain an image as complete as possible of the influence of the H₂SO₄ concentration on the coverage degree of the titanium surface with Ti-oxide.

Table 4. Coverage degree of titanium electrode surfaces with oxide in various concentrations of H₂SO₄ solutions on constant potentials.

<table>
<thead>
<tr>
<th>H₂SO₄ concentration</th>
<th>Coverage degree, θ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E=0.5 V</td>
</tr>
<tr>
<td>1.5 M</td>
<td>98.24</td>
</tr>
<tr>
<td>1 M</td>
<td>98.32</td>
</tr>
<tr>
<td>0.5 M</td>
<td>98.82</td>
</tr>
<tr>
<td>0.1 M</td>
<td>98.04</td>
</tr>
<tr>
<td>0.05 M</td>
<td>88.60</td>
</tr>
</tbody>
</table>

Based on these results, it can saw that as the potential increases, there is a decrease in the surface coverage degree, indicating the occurrence of the dissolution of the titanium oxide films. It can also saw that with the lowering of acid concentration, the degree of oxide surface coverage falls, which indicates the fact that with the increase of H₂SO₄ concentration, the oxide formation on titanium surface unfolds faster.

4. XRD and EDS analyses of anodized and annealed Ti substrates in H₂SO₄

XRD and SEM-EDS recordings show the indisputable presence of Ti-oxides in the anodized oxide layer. This oxide layer forms on the surface of the titanium electrode in 3M H₂SO₄.

The light yellow color of anodizing anatase crystals TiO₂, from acidic solutions, is the most common crystalline TiO₂, as said before. The anodization of Ti and getting of thick TiO₂ films before modification of titanium surface with mixed platinum metal oxides is not a good recommendation because of possible anode passivation. For some titanium applications, such as DSAs (Dimensionally Stable Anodes) preparation, thick layers lead to electrode passivation. However, the presence of TiO₂ on the surface is necessary for better adhesion and stabilization of the electrocatalytic oxides layer. The TiO₂ protecting films are permanently rebuilding when the electrodes are polarized anodically. The different deactivation mechanisms of DSAs can be the passivation of titanium substrate, coating detachment, and mechanical damages, which should consider in the production and application of these anodes.

Different ways of making DSAs with mixed metal oxide (MMOs) layers often involve using a thermal treatment, and it is the electrode annealing at different temperatures. For this reason, it has been necessary to study the behavior of the anodized Ti substrate, followed by annealing at 400 °C (characteristic annealing temperature for TiO₂ crystals of the anatase type).

Figure 5. shows the XRD image of the Ti substrate after anodization in 3 M H₂SO₄ and after annealing sample at 400 °C in the airflow, previously prepared in the same way.

According to the results present in Figure 5. crystalline TiO₂ has formed by anodization of titanium in various
concentrations of H$_2$SO$_4$. The intensity of peaks for the anatase type of crystals also suggests a thin TiO$_2$ film formation. The height of the same peaks increases after the annealing titanium electrode at 400 °C, which indicates that the oxide film of anatase becomes thicker after heat treatment.

SEM-EDS analyses (Figure 6.) confirm the results obtained by XRD measurements. It can also observe that after anodization on the titanium surface Ti and O$_2$ species exist. This suggests the formation of an oxide layer on the electrode surface. According to chemical analysis, after annealing of titanium, the content of O$_2$ species increase indicates thicker TiO$_2$ oxide films (Table 5.).

**Table 5.** Chemical composition of titanium surface after anodization in 3 M H$_2$SO$_4$ and after annealing at 400 °C at a time of 1 h.

<table>
<thead>
<tr>
<th>Atomic species</th>
<th>O %</th>
<th>Ti %</th>
<th>Total %</th>
</tr>
</thead>
<tbody>
<tr>
<td>after anodization</td>
<td>17.30</td>
<td>82.70</td>
<td>100.00</td>
</tr>
<tr>
<td>after thermal treat.</td>
<td>28.40</td>
<td>71.60</td>
<td>100.00</td>
</tr>
</tbody>
</table>

**Figure 5.** XRD patterns of Ti electrode: A) after anodizing in 3M H$_2$SO$_4$, B) after annealing the anodized Ti electrode, at 400 °C in the airflow.

**Figure 6.** SEM-EDS images of A) Ti electrode after anodizing in 3M H$_2$SO$_4$, B) annealed Ti electrode at 400 °C 1 h after anodizing in 3M H$_2$SO$_4$.

5. CONCLUSIONS

The formation of oxides on the surface of titanium in H$_2$SO$_4$ solutions carried out over a wide range of potentials. According to the results obtained, and characterization of formed oxide films observed several conclusions. TiO$_2$ is the most stable formed oxide, but TiO and Ti$_2$O$_3$ oxides are also formed by anodization from solutions investigated. The results obtained during CV measurements also indicate the rapid formation of an oxide layer with variations of the stoichiometry and morphology on the titanium surface.

Open circuit potential and potentiodynamic measurements indicate that there is generally no significant deviation in the oxidation process and the forming of the oxide film on the Ti and (Ti+TiO$_2$)-electrode surface. Based on the results of the potentiodynamic measurements, it can saw that the formation of the oxide films is initiated at the very beginning of the polarization process. Furthermore, passivation of the titanium surface occurs because of the growth of the surface oxide layer and surface leveling.

XRD and SEM-EDS analyses confirmed the presence of titanium oxide films on the titanium anode. After thermal treatment of the electrode, XRD recordings showed a higher intensity of anatase peaks in the anodized oxide films. SEM-EDS recordings also confirmed the higher presence of oxides on the thermally treated titanium electrode. The appearance of the anatase structure of crystals in the oxide film was also certified.

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