Electropolishing of Titanium and Titanium Alloys in Perchlorate-Free Electrolytes

By O. Piotrowski, C. Madore & D. Landolt

A new perchlorate-free electrolyte electropolishing process for titanium and titanium alloys has been developed, using a sulfuric acid-methanol mixture as electrolyte. Electrolyte composition and polishing conditions were optimized by measuring current-voltage curves on a rotating disk electrode at temperatures of -10 to 25 °C. Mass-transport-controlled limiting current plateaus were observed for sulfuric acid concentrations between 2 and 4 M. Best polishing was obtained in an electrolyte containing 3 M sulfuric acid at an applied potential of 8 V against a saturated mercurous sulfate reference electrode. The topography of the polished surfaces was characterized by optical microscopy, optical profiling and by atomic force microscopy.

Titanium and titanium alloys are lightweight structural materials with good corrosion resistance. Because of their chemical inertness, they find numerous applications in the chemical process industry and for medical implants. The biocompatibility of titanium has been attributed to the thermodynamically and mechanically stable oxide layer that forms spontaneously on the surface.[1] In recent years, there has been an increasing demand for bright and polished titanium surfaces for objects of often complex shape. For such applications, electrochemical polishing processes are promising in view of their flexibility and cost-effectiveness.

Electropolishing is defined in a general way by ASTM[2] as the improvement of surface finish of a metal effected by making it anodic in an appropriate solution. A review of the electrochemical conditions leading to electropolishing of metals has been given by Landolt,[3] and practical aspects have been treated by Tegart.[4] Electropolishing of titanium is normally carried out in acid media containing perchlorate ions, a typical example being concentrated acetic acid-perchloric acid mixtures.[5-11] A few perchlorate-free electrolytes for electropolishing of titanium have also been proposed,[12-15] but they normally contain either fluoride or chloride ions to facilitate attack of the passive oxide film. Table 1 gives an overview of electrolyte formulations for electropolishing of titanium proposed in the literature. A common feature of these electrolytes is their relatively low water content. A high water content tends to increase the chemical stability of the passive oxide film formed on the titanium surface. Anodic polarization in such a case leads to dissolution by pitting rather than to polishing.[3]

The role of oxide films in electropolishing of titanium in acetic acid-perchloric acid electrolytes has been studied previously in our laboratory.[8,9] To achieve polishing conditions, anode potentials in excess of 20 V are needed for the anodic oxide film to break down.[8] Perchlorate-based electrolytes are well suited for small scale applications, such as preparation of samples for electron microscopy, but their use for large scale industrial applications poses a safety hazard.

In addition, perchlorate or chloride-based electrolytes can cause a chloride contamination of the polished surface.[8] Rambert *et al.*[16] showed that titanium boride can be electropolished in sulfuric acid-methanol-based electrolytes provided suitable conditions can be found that correspond to a mass-transport-controlled dissolution. In the present study, a similar approach is applied to the development of a perchlorate-free electrolyte for electropolishing of titanium and titanium alloys. Using a rotating disk electrode, anodic polarization curves are measured as a function of electrolyte composition, rotation rate and temperature to find conditions under which anodic dissolution of titanium is mass-transport-controlled. Polishing experiments are then carried out and the surface topography is characterized by electron microscopy and surface roughness measurements.

Experimental Procedure

The electrochemical cell consisted of a jacketed glass vessel containing one liter of electrolyte solution. The experiments were performed using a rotating disk electrode machined from commercially pure titanium rods (Ti 99.6%) 5 mm in diameter (surface area 0.20 cm^2), embedded in an epoxy insulation, with 10 mm outer diameter. Prior to each experiment, the working electrode was polished with a 600 grit emery paper, rinsed with ethanol and doubly distilled water and dried. The counter-electrode was a platinum wire (Pt 99%), separated from the working electrode by a glass sleeve. A saturated mercurous sulfate reference electrode placed far from the working electrode was used. All potentials given herein refer to this reference electrode. No IR correction was applied to the measured polarization curves.

A potentiostat, controlled by an interface, was used. Polarization curves were measured by sweeping the potential from 8 V to 0 V, using a scan rate of -10 mV/sec. It was found necessary to sweep the potential from positive values in the cathodic direction in order to obtain reproducible measurements and to avoid pitting of the electrode surface.

Electrolytes were made by slowly adding sulfuric acid (96%) to methanol. The sulfuric acid concentration in the methanol solution was varied from 0.5 M to 5 M. The temperature of the electrolyte was maintained at 25, 0 or -10 °C by a cryostat. The electrode surface topography resulting from dissolution was characterized by optical surface profiling, optical microscopy, atomic force microscopy (AFM) and, in some cases, scanning electron microscopy (SEM).

Results and Discussion
Potential Sweep Experiments

Polarization curves measured at sulfuric concentrations of 0.5, 3, and 5 M are shown in Fig. 1. The electrolyte temperature was 25 °C. The results show that the shape of the polarization curves is strongly influenced by the sulfuric acid concentration. No limiting current plateau is observed when
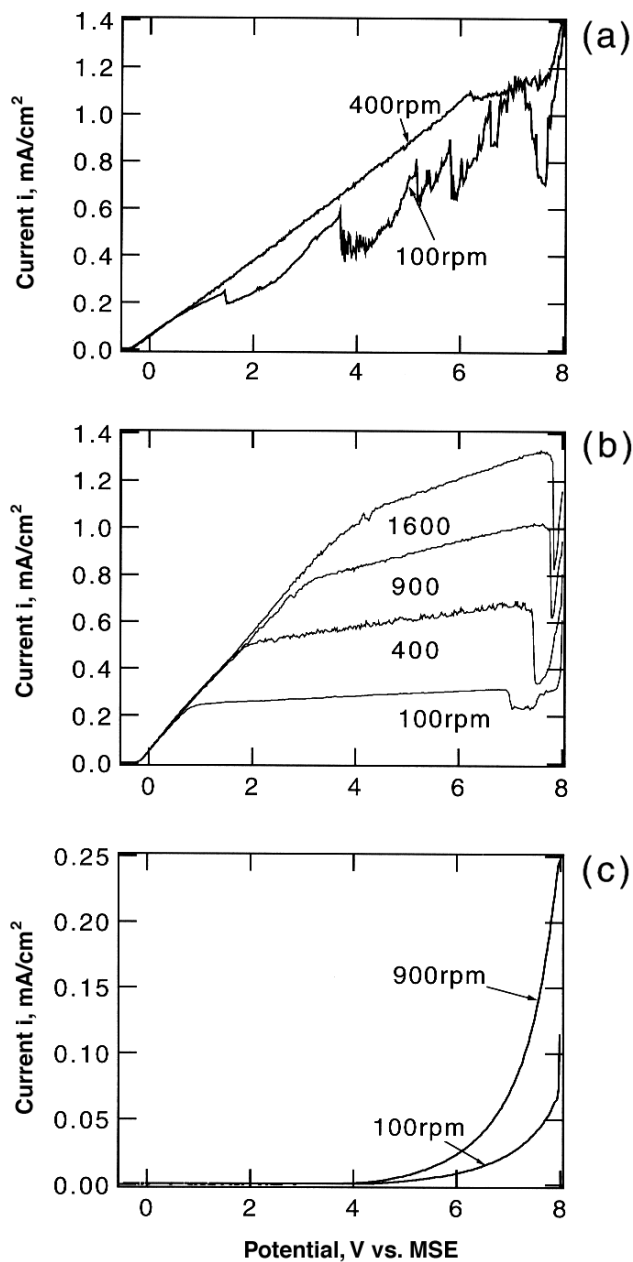
Fig. 1—Potentiodynamic polarization curves determined for titanium in methanol-based electrolyte containing (a) 0.5 M H₂SO₄, (b) 3 M H₂SO₄, and (c) 5 M H₂SO₄ Temp 25 °C.

Fig. 2—Potentiodynamic polarization curves determined for titanium in the electrolyte containing 3 M H₂SO₄ in methanol at (a) 0 °C and (b) -10 °C.

the electrolyte contains 0.5 M sulfuric acid (Fig. 1a). The current density varies almost linearly with potential, suggesting that the current-voltage behavior is dominated by the ohmic resistance in the electrolyte. Some gas bubbles were observed at the electrode surface during the experiment, causing fluctuations in the measured current density. The electrode felt hot after completion of the experiment. This suggests that the gas observed may have resulted from boiling of the electrolyte resulting from joule heating because of the large voltage drop at the interface. No polishing was obtained under the conditions of these experiments. For an electrolyte containing 3 M sulfuric acid, on the other hand, large limiting current plateaus were observed extending from 8 V to 2 V, approximately, at all rotation rates. The magnitude of the measured current densities in the plateau region increased with increasing rotation rate and decreased with increasing sulfuric acid concentration (not shown in the figure).
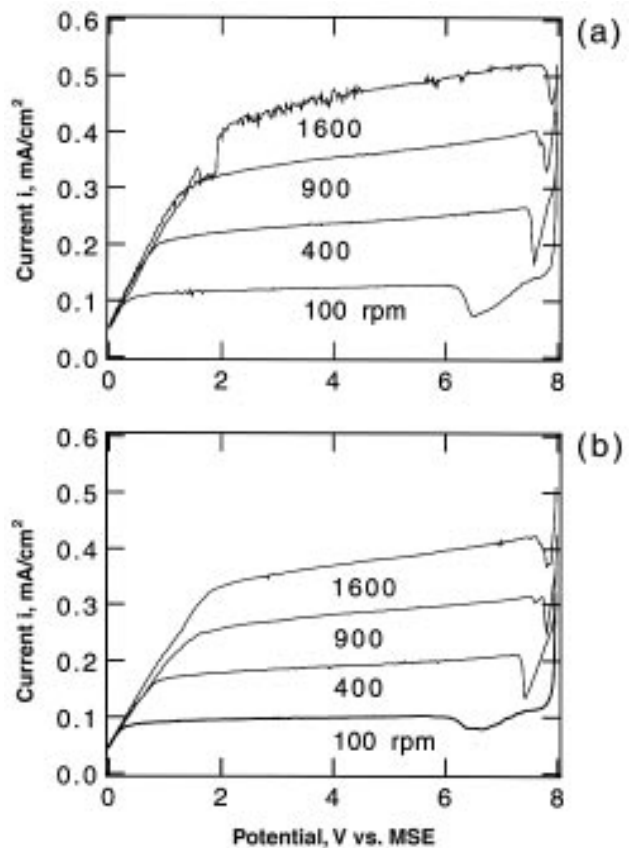
In Fig. 1b, a distinct minimum in current is present between 7 and 8 V. It results from the formation and subsequent detachment of an anodic film. The time needed for the film to detach from the electrode surface (and hence the position of the minimum on the potentiodynamic polarization curve) depended on the electrode rotation rate, a high rotation rate enabling reduction of the time for film detachment. Under limiting current conditions, no visible film was present on the surface; the electrode surfaces observed after an experiment appeared bright and polished to the naked eye. When the concentration of sulfuric acid was increased to 5 M (Fig. 1c), the film formed at the beginning of a sweep no longer became detached from the surface. Rather than going through a minimum, the current decreased with decreasing potential to very small values. The surface of the electrode after dissolution appeared yellowish as a result of the presence of a surface film. No polishing was observed in this case.

To study the effect of temperature, experiments were carried out in the 3 M H₂SO₄ electrolyte at 0 and -10 °C. Figure 2 shows polarization curves measured at different rotation rates. They all exhibit a well-defined limiting current plateau, with the limiting current density decreasing with decreasing temperature. Figure 3 shows the reciprocal of the limiting current density plotted against the reciprocal of the square root of the rotation rate. For a mass-transport-limited reaction at a rotating disk electrode, such a plot should yield straight lines going through the origin.[17] The results of Fig. 3 confirm that the reaction rate at the limiting current was

Table 1
Polishing Electrolytes for Titanium

	Reference								
Reagent	5	6,7	8,9	10	11	12	13	14	15
$HClO_4$ 70%	185 cm³	60 cm³	10 cm³	200 cm³	30 cm³				
Acetic anhydride	795 cm³								
Acetic acid		1000 cm³	100 cm³						
Methanol						300 cm³		200 cm³	
Ethanol			350 cm³			90 cm³			
Butanol					175 cm³	10 cm³			
Glycerol			100 cm³						77%
H_3PO_4							800 g/L		
H_2SO_4							80 g/L	10 cm³	
HF									3%
H_2O	48 cm³							7 cm³	10%
$AlCl_3$ anhydrous						6 g		8 g	
$ZnCl_2$						28 g		5 g	
KH_2PO_4							15 g/L		
$NaHPO_4$							15 g/L		
NH_4F									5%
NH_4NO_3									5%

indeed mass-transport-controlled. The data suggest that within the range studied, polishing conditions can be obtained at all temperatures. To minimize surface heating and to avoid high anodic current densities, it is generally preferable, however, to work at low temperature.

Dissolution Stoichiometry

The apparent valence of dissolution of titanium at the limiting current was determined by carrying out dissolution experiments at different potentials at a rotation rate of 900 rpm and

Polishing Experiments

Polishing experiments were performed potentiostatically in the 3 M sulfuric acid electrolyte at an electrode rotation rate of 400 rpm. The electrolyte temperature was -10 °C, yielding a limiting current density of 0.2 A/cm². Under these conditions, no appreciable heating of the anode surface was observed. Commercially pure titanium and two titanium alloys, Ti6Al4V (89% Ti, 6% Al, 4% V) and Ti6Al7Nb (86% Ti, 6% Al, 7% Nb), were used. Prior to electropolishing, the electrode surface was mechanically polished with a 600 grit emery paper. A charge corresponding to 60 °C was passed in all experiments. In Fig. 4, a typical current transient observed in potentiostatic polishing experiments is shown for an applied potential of 8 V. Initially, upon application of a constant anodic potential, the current density decreases because of
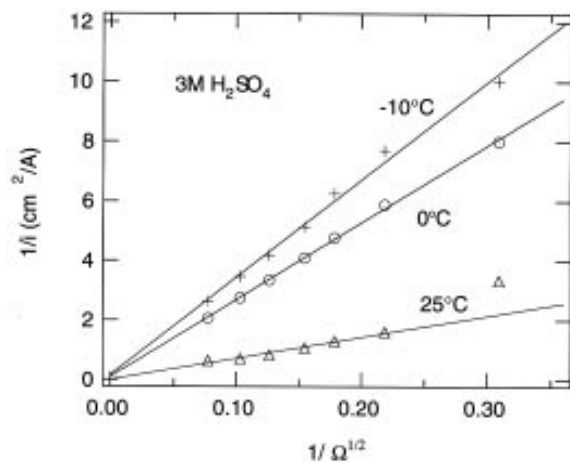

Fig. 3—Relation between the reciprocal of the limiting current density and the reciprocal of the square root of the rotation rate determined for titanium in the electrolyte containing 3 M H_2SO_4.
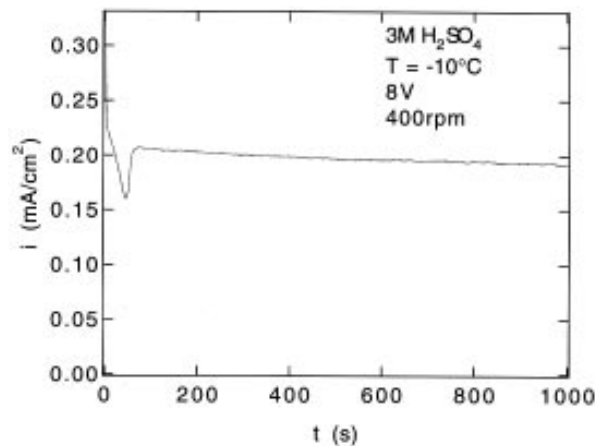

Fig. 4—Current transient determined for titanium polarized at 8 V in the electrolyte containing 3 M H_2SO_4 at -10 °C and for rotation rate of 400 rpm.
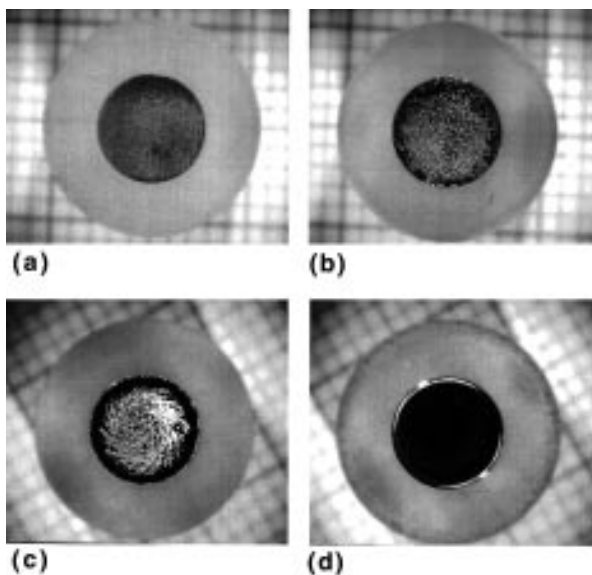
Fig. 5—Optical micrograph images of titanium surfaces (a) mechanically polished with 600 grit emery paper, electropolished at (b) 2 V, (c) 6 V, and (d) 8 V. Electropolishing was performed in the 3 M H₂SO₄ electrolyte at -10 °C and for rotation rate of 400 rpm.

Table 2
Valence of Dissolution for Titanium
(in 3 M H_2SO_4 methanol solution, 25 °C, 900 rpm, charge 60 °C)

Applied potential, V	Weight loss, mg	Valence
8.0	2.4	4.1
7.0	2.5	4.0
6.0	2.4	4.1
5.0	2.3	4.3
4.0	2.5	4.0
2.0	2.6	3.8

Table 3
Average Roughness Ra of Polished Titanium
& Titanium Alloy Surfaces
(determined by UBM)

Surface	Ra, μm
Ti mechanically polished	0.052 ±0.003
Ti electropolished (8 V, -10 °C)	0.033 ±0.003
Ti6Al4V electropolished (8 V, -10 °C)	0.056 ±0.003
Ti6Al7Nb electropolished (8 V, -10 °C)	0.061 ±0.033

formation of an anodic film. After about 100 sec, it increases abruptly, indicating that the anodic film has become unstable and permitting its removal by the fluid flow. The current density reaches a quasi-steady state corresponding to dissolution under polishing conditions. The slight decrease of the current density with dissolution time is probably a result of recession of the surface, which may reduce the transport rate to the disk.[18]

The effect of potential on the surface morphology of pure titanium dissolved under limiting current conditions is shown in Fig. 5. At a potential of 2 V (Fig. 5a), situated at the beginning of the limiting current plateau, the surface exhibits several bright pits, while some parts of it are covered with a dark film. At 6 V (Fig. 5b), the surface becomes brighter and the pits are smaller. Some waviness, corresponding to the hydrodynamic flow pattern on rotating disk electrodes can be seen. A bright and smooth surface is obtained at 8 V (Fig. 5c). The data shown indicate that good electropolishing can indeed be obtained with the present electrolyte under limiting current conditions. On the other hand, they also demonstrate the importance of applied potential in the plateau region. Observation of a limiting current plateau, therefore, is not a sufficient criterion for obtaining good electropolishing of titanium.

Figure 6 compares the roughness profiles measured with an optical profilometer on the electropolished surfaces described above. The average roughness decreases significantly with increasing potential, as shown by the values of Ra given in Table 3. They were evaluated following the norm, DIN 4768 (*i.e.*, five traces were measured, starting from a common origin, using an effective measurement length of 4 mm and a high pass filter with a cut-off of 0.8 mm). In Table 3, measured Ra values for Ti6Al4V and Ti6Al7Nb, electropolished at 8 V under identical conditions as pure titanium are also shown. The average roughness for pure titanium is about 0.03 μm, that of the titanium alloys 0.05-0.06 μm. The latter value compares favorably with the roughness obtained by careful mechanical polishing of titanium. The atomic force microscope was used to further characterize the surface morphology of the pure titanium surface electropolished at 0.8 V. Figure 7 shows a three-

dimensional representation and the corresponding roughness profile. The results confirm the absence of crystallographic etching, resulting in a very smooth surface topography. The largest amplitudes of the roughness profile are on the order of 10 nm only. The origin of the white spots appearing on the AFM picture is not known and they could be a result of measurement artifacts, inasmuch as no similar features were observed with the scanning electron microscope.
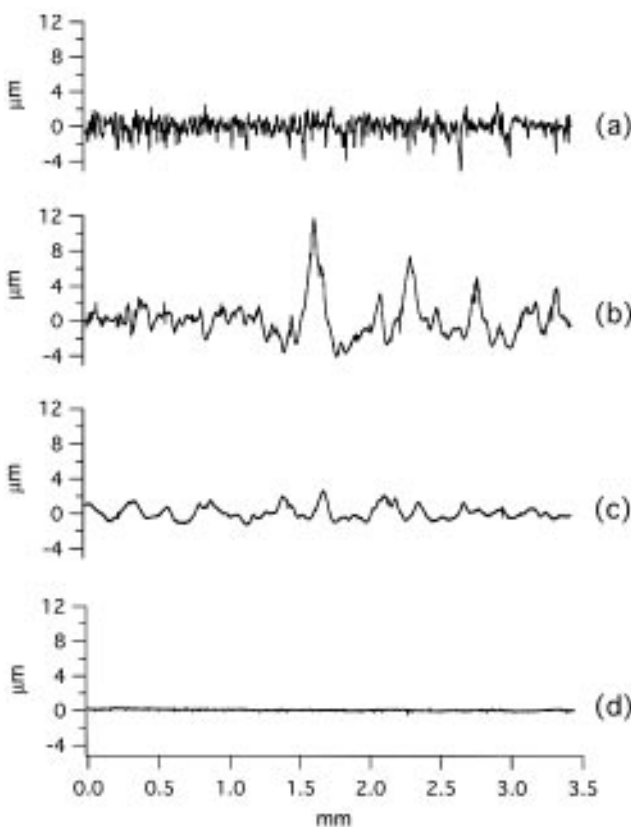

Fig. 6—Roughness profiles measured with optical profilometer of titanium surfaces (a) mechanically polished with 600 grit emery paper, electropolished at (b) 2 V, (c) 6 V, and (d) 8 V. Electropolishing conditions as in Fig. 5.
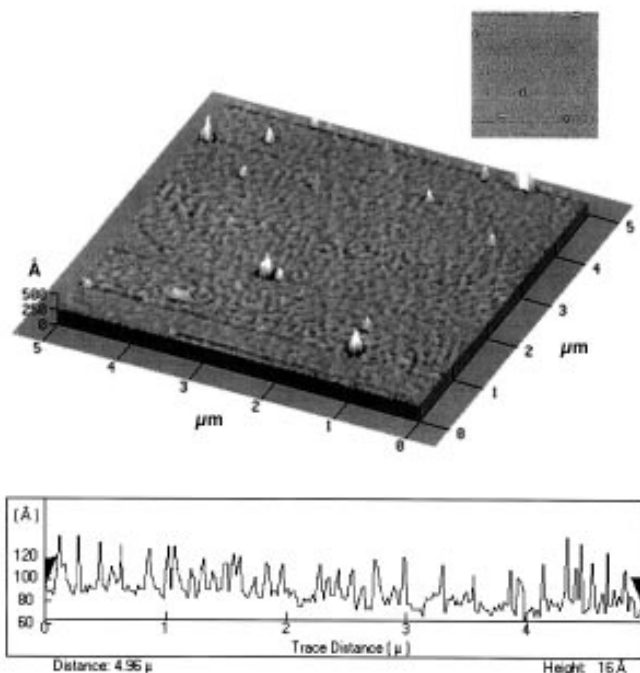
Fig. 7—AFM image of the titanium surface electropolished at 8 V. The corresponding roughness profile is also shown.

Summary and Conclusions

Electropolishing of pure titanium and two commercial titanium alloys has been achieved in a perchlorate-free electrolyte based on a mixture of methanol and sulfuric acid. To optimize polishing conditions a rational approach was used, based on the observation that electropolishing generally occurs under mass-transport-controlled conditions.[3] Microscopic study of the resulting surface topography indicated that within the limiting-current plateau region, the applied potential also plays an important role for the resulting surface finish. The origin of this interesting observation and the underlying mass transport processes are now being investigated in our laboratory, using impedance spectroscopy and other methods. Under optimum conditions, the average surface roughness achieved for titanium in the current electrolyte was Ra = 30 nm, a factor of two better than that achieved by mechanical polishing. Under the same conditions, a value of Ra = 60 nm was achieved for the titanium alloys Ti6Al4V and Ti6Al7Nb. The electropolishing process described in this paper is therefore applicable to titanium alloys as well as to pure titanium. At the present time, a scale-up of the described polishing process to surface finishing of objects of complex shape and large surface area has not yet been achieved, one reason being the described heating problem. On the other hand, the process has been found well suited for surface structuring and micromachining of titanium through photoresist masks, an application which at present is being developed successfully in our laboratory.[19]

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