

# Electropolishing

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Electropolishing of metal surfaces is a benign alternative to mechanical treatment. Ionic liquids are considered as green electrolytes for the electropolishing of metals. They demonstrate a number of advantages in comparison with acid aqueous solutions and other methods of producing smooth or mirror-like surfaces that are required by diverse applications (medical instruments, special equipment, implants and prostheses, etc.).

Keywords: polishing ; electropolishing ; ionic liquid ; molten salt ; metals and alloys ; treatment of metal ; anodization

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## 1. Introduction

Anodic treatment is one of the most effective methods used in the finishing of metals and alloys to achieve a mirror-like state of the metal surface. The result of this process depends on a number of factors, including the properties and composition of metal and electrolyte, temperature, voltage, current density, time, and others <sup>[1][2][3][4][5][6][7]</sup>.

There are various industrial applications requiring a particular quality of the metallic surface. Anodization results in different types of changes to the metal surface, such as etching, pitting, deflashing, passive film formation, nanostructure self-organization, deburring, trimming, smoothing and so on.

Anodization of metals and alloys has been studied in detail in aqueous solutions of various electrolytes <sup>[8]</sup>. However, water is electrochemically active at potentials of discharge of the majority of metals and can also take part in electrode reactions. On the other hand, ionic liquids <sup>[9]</sup> (IL) demonstrate larger electrochemical windows and are already used as electrolytes in medicine and industry <sup>[10]</sup>.

## 2. Electropolishing Mechanisms

The light reflectance of the surface is known to be the immanent property of any metal. The majority of metals are strong reductive agents. Metals exposed to environmental molecular oxygen, water vapor, carbon dioxide, and so on form superficial oxides, hydroxides, nitrides, and salts, diminishing the reflectivity. The metal surface becomes dull due to the superficial films of these compounds. The tarnish of the metal surface is determined by both the properties and thickness of the superficial films. A film-free surface of the metal, for example, after mechanical treatment (abrasion), also reflects visible light well enough. The high reflectance of the mechanically polished metal surface is due to a great difference between the linear sizes of the superficial defects (< 1–10 nm) and the wavelength of the visible light (400–800 nm) <sup>[11][12]</sup>. When the wavelength of the visible light is near or greater than the sizes of asperities, the metal surface seems dull.

The metal surface dimness diminishing the reflectance in the optical region is essentially due to the light scattering on the film rather than on the defects of the metal surface. The surface light scattering is dependent on the ratio of the light wavelength and sizes of oxide film roughness.

Effective light scattering of oxidized surfaces is observed for many metals. Aluminum is a typical example proving this phenomenon. The aluminum oxide film is assumed to produce a dull finish on the metal surface, owing to its considerable thickness (~0.5–1 μm) <sup>[13][14]</sup>. The light scattering on natural oxidized copper is also due to the oxide film, the thickness of which was calculated to be about 627 nm <sup>[15]</sup>. The oxide film thicknesses on chromium <sup>[16]</sup>, nickel <sup>[17]</sup>, and titanium <sup>[18][19]</sup> are considerably smaller (3–7 nm) than the wavelength of visible light. That is why metallic Cr, Ni, and Ti maintain the high brightness of their naturally oxidized surfaces.

Smoothing to obtain a mirror-like metal surface implies, first of all, a removal of metal oxide excess. Mechanical treatment of the oxidized metal surface (e.g., abrasion, buffing, burnishing, etc.) may be successfully used to give workpieces a high polish. On the other hand, chemical dissolution of the superficial compounds based on the reaction with acids does not

always lead to a mirror-like metal surface, because of nonselective action of hydrogen ions. In most cases, acidic treatment results in etching or pitting of the metal surface [20].

A glossy metal surface can be formed by both anodic and cathodic polarizations of electrodes. A wide-spread cathodic reduction does not refer to the electropolishing processes. Usually, electrochemical polishing is considered as an anodic reaction. Electrochemical oxidation provides an alternative way to achieve the required result. An anodic polarization of a metal electrode to be focused on electropolishing imposes certain requirements for the chemical nature of the electrolyte, which must be, first of all, stable enough at the potentials applied. Aqueous solutions of strong electrolytes hardly fulfill these requirements. The use of aqueous solutions is evidently restricted in the fabrication of mirror-like surfaces of metals or alloys on account of the competitive side-reaction of water oxidation to molecular oxygen (Equation (1)) [3].



Although water is a less active reducing agent compared with base metals, the probability of Equation (1) in aqueous solutions is high enough. Electrochemical oxygen evolution favors the appearance of secondary metal oxide films. Only a minority of metals can be polished to a bright surface by anodization in aqueous solutions of acids. These metals should be inert to acids and should be covered with thin passive oxide films (stainless steel, nickel, copper, platinum, etc.). The result of electropolishing for the majority of the industrially important metals in acid solutions is etching or pitting. Electropolishing being targeted at the fabrication of a mirror-like metal surface implies a dissolution of oxide films as the main reason for diffuse light scattering.

Electrochemical oxidation of water evidently occurs on the metal surface due to the diffusion of water molecules within the pores of the oxide layer.  $\text{H}^+$  ions, being electrochemically formed, move in a reverse direction towards the cathode and may react with metal oxide according to Equation (2). The migration rate of the hydrogen ions to the cathode and the thickness of the oxide film determines the probability of the occurrence of the heterogeneous chemical Equation (2) providing the dissolution of the oxide film.



The probability of Equation (2) clearly decreases with the increase in the  $\text{H}^+$  migration rate to the cathode. The  $\text{H}^+$  migration rate depends on the viscosity of the electrolyte; the porosity, thickness, and chemical properties of the oxide film; as well as temperature, current density, voltage, and other factors [1][2][3]. If the electropolishing occurs in acidic solutions, Equation (2) becomes the main process [1][3][4][5].

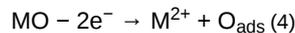
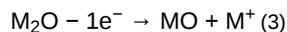
In recent years, ionic liquids [10][21][22][23] tend to be actively used as electrolytes for a lot of electrochemical processes. Ionic liquids are of growing interest due to their outstanding advantages against aqueous solutions. Electrochemical potentials of discharge of the ionic liquid ions are significantly shifted to larger values (electrochemical window) that exclude all side reactions with the solvent participation.

Among a set of industrial processes, electropolishing of metals and alloys is known to be particularly sensitive to the chemical nature of the electrolyte. There are diverse areas that require mirror-like metal surfaces (e.g., microelectronics [24], construction of space technics and aerospace frames [25], medical instruments [26][27], biocompatible alloys [28][29][30][31][32][33], and others). Electropolishing of metals and alloys is similar in its function to dissolution during the passage of current to provide the removal of the surface roughness and to achieve a smooth surface.

The upper layers of the surface of base metals and alloys are known to consist of natural oxide films of different compositions covering crystalline metal defects. The metal surface smoothing to obtain a brilliant reflectance is a sequence of complex processes, including not only the removal of metal oxides, but also the controlled elimination of defects of the surface. It is evident that electrochemical removal of oxide films and metal roughness represents different consecutive processes taking place at the interface of the electrode.

Electropolishing efficiency is dependent on the chemical properties of the films, which are known to be individual for each metal or alloy. In general, the mechanism of metal surface electropolishing implies discrepant rates of the removal of covering films and proper metal atoms from different sites of the surface. The oxide films are often removed owing to Equation (2), both in aqueous and non-aqueous solutions. In the latter case, hydrogen ions appear after anodic oxidation of residual water. After oxide film removal, the smoothing of the surface occurs with a higher current density on the edges of the crystal structure.

A chemical dissolution of the superficial oxides according to Equation (2) is not the sole process of oxide film removal. In the absence or lack of hydrogen ions (e.g., in ionic liquids), the electrochemical dissolution of oxides becomes more probable and may undergo one/two-electron processes (Equations (3) and (4)) [15].



Equations (3) and (4) are competing with Equation (2) in IL, particularly for the low-valence metals (copper, tin, lead, etc.).

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