

Electropolishing

Electrolytic brightening, smoothing and deburring
of stainless steel, steel, brass, copper, aluminium,
titanium and magnesium

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and 3 tables



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Said in one sentence,
the chemical equilibrium
seems to be an expression
for the end of any chemical reaction.
after van't Hoff

Foreword

After dealing with many questions on electropolishing I was asked to write a book on this subject by Eugen G. Leuze Verlag KG. In 2009 the German version of this book was published [BUHL, 2009a]. It found its readers in the electrochemical community. Since I wrote my theses and many articles on electropolishing and the dynamics of the electrochemical metal removal there was the wish to publish a book on the subject to give a wide overview on this manufacturing technique.

This book was only possible, because I had the chance to work in the group of Prof. Dr. Andreas Visser at the University of Bremen. Subject of my research in his lab was the electrochemical removal of metals by etching and electropolishing. The same importance for this work had my stay in the group of Prof. Dr. Peter Jörg Plath at the chemical department of the university. There I dealt with questions of the non-linear dynamics of the electrochemical removal of metals. The one and the other were necessary to get the knowledge which is the basis for this book. I deeply thank both for their teaching and inspiration. My hope is that this book is a help to understand electropolishing better.

Due to electropolishing it is possible to furnish smooth and shining surfaces of many metals. Therefore this manufacturing technique can be used for many purposes. I hope this book will help to spreading applications for this technique. Since the knowledge on this topic is little the mission of this book and its German version is to widen it. The interesting manufacturing process deserves to be considered more often.

I hope the readers will enjoy this book. Also I wish that the book will be a help to solve some of their technical problems and answer scientific questions.

Bremen, June 2015
Magnus Buhlert

1 Introduction

Smooth and bright shining metal surfaces can be made by electropolishing. The manufacturing procedure can be described as anodic, electrolytic or electrochemical removal process with outer power supply. According to the goal of the manufacturing process electropolishing can be named as electrolytic or anodic brightening, smoothing, cleaning or deburring. Electropolished surfaces are characterised by their low specific extension and their enhanced corrosion resistance. They can be cleaned more easily and buds adhere badly. It is used to smooth and to clean surfaces by electropolishing before galvanisation. In addition the process can be use for deburring metallic workpieces.

The process is used in tank and pipeline construction. In the beverage and food industry as well as in the pharmaceutical industry the outstanding properties of electropolished surfaces come into account. Even in medical technique the process is used. Implants are electropolished, if smooth surfaces and pieces without sharp edges are needed. Therefore stents are electropolished often. Electropolishing is used for decorative purposes in cases where brightness and metallic appearance comes into play. Even in material sciences electropolishing or similar anodic removal processes are used to prepare metallic samples.

Depending on the desired properties of the surface, the process parameters have to be optimized. For many metals and their alloys one will find electropolishing techniques described in literature. They can be transferred to comparable alloys and materials, even if a new optimization of the process parameters will be necessary most of the time. The choice of the process or the starting point of and optimization depends on the chemicals needed. What was used in former times is not always allowed or best choice today. The legislation changed and the knowledge on the hazards of chemicals grows. Therefore one always should look for processes with less hazardous or environmental effects. Materials and chemicals should be preferred, that lead to less harm for employees and environment, if used in the right way. Besides the choice of the right chemicals for a given material it is necessary to have skilled persons to handle the electrochemical removal process in the lab or even in manufacturing.

In this book you will find, what I could carry out with experiments together with others, my own experience on the topic and what can be found in the newer literature on the matter. Basis for this book are several own publications on electropolishing an electrochemical removal among them my doctoral thesis about electropolishing and the dynamic of the electrochemical removal of metal and the German version of this book. In other words: This book is the rewritten version of the German one.

After a short look on the manufacturing process and the general relations of process parameters and manufacturing result the influence of the main parameters of the process are discussed. Different possible manufacturing steps and their benefits are discussed. Further different electrolytes for different metals respectively alloys can be found. At least some manufacturing results for some combinations of metals and electrolytes are given.

2 Removal Process

2.1 Characteristics of the removal process

The surface of a metallic workpiece is removed electrochemically during electropolishing. Workpieces are brightened, smoothed or deburred in this way. In opposite to etching and chemical brightening an external power supply is needed to remove metal ions electrolytically during electropolishing. Aim of the process is the removal of metal. Therefore electropolishing belongs to the removal processes. In difference to other electrochemical manufacturing processes the shape of the workpiece is not changed by electrochemical polishing. As the surface is removed the process belongs to the surface finishing processes.

2.2 Electrochemical Reactions

2.2.1 Anodic Reactions

Within this chapter the overall anodic reactions of the electrolytic smoothing or brightening process are described. The valence of the dissolved metal ions is of importance for the calculation of the efficiency of the removal reaction. At first the overall reactions of the removal reactions are given. After that the oxygen evolution at the anode during transpassive electropolishing is discussed.

2.2.1.1 Classical idea of metal removal

Before the overall reaction is presented, some words are spend on the classical idea of the removal of metals by electrochemical means. Weather this idea fits somehow for highly concentrated solutions or not, is not clear up to now. It is still under investigation by others. It can be assumed that in case of highly concentrated electrolytes the removal process is much more complicated or even complex. How far the classical idea can be transferred on the electropolishing process using highly concentrated electrolytes is not fully investigated. There are still many open questions. As theories of the electrochemical removal in high concentrated solutions are missing the behaviour in normal electrolytes still helps to understand the process.

After Kaesche [KAE, 1979] the electrochemical removal of metals takes place in some steps. The different steps are illustrated in *Figure 1*. In the first step the surface atoms leave

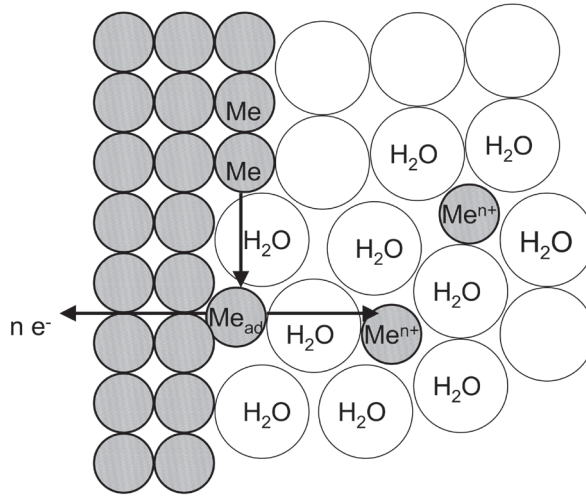


Fig. 1: Dissolution of metals via adsorbed ions to hydrated ions

the lattice and are transformed into adsorbed atoms. These adsorbed atoms are no longer immobile. They are sideward mobile on the metal surface.



Thereafter the atom passes the electrochemical doublelayer, loses valence electrons and becomes in ion.



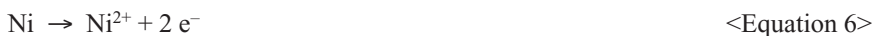
If metals have more than one oxidation step, the valence electrons are spend stepwise. Copper for instance is oxidised to Cu^{+} first. After that it is further oxidised to Cu^{2+} [HAM, 1985].

In a further step the metal ions are transported into the solution itself. This is done by migration, diffusion and convection. In aqueous solutions ions hydratise. They are covered or surrounded totally by water molecules.



2.2.1.2 Stainless Steel and Steel

Usually mixtures of sulphuric and phosphoric acid and water are used for electrochemical brightening and smoothing of stainless steel. Iron and chromium dissolves trivalent in this kind of electrolyte. Nickel dissolves bivalent [BUHL, 2000]. The overall reactions are:



Several investigations show, that steel can be electropolished in the same electrolytes as stainless steel [BUHL, 2003k; BUHL, 2003l; BUHL, 2004a; BUHL, 2004h]. It can be assumed that the same over all reactions take place in this case.

2.2.1.3 Brass and copper

During electropolishing of copper in aqueous solutions of phosphoric acid and alcohols it dissolves bivalent. The reaction may have several steps. During electropolishing brass copper and zinc dissolve bivalent as well [BUHL, 2000].



2.2.1.4 Aluminium

Aluminium dissolves in aqueous solutions of phosphoric and sulphuric acids trivalent. Magnesium dissolves bivalent [BUHL, 2000].



2.2.1.5 Magnesium

Magnesium and its alloys can be electropolished in mixtures containing mineral acids. Described are aqueous electrolytes of phosphoric acids and alcohols [SCHMIDT, 2012]. It dissolves bivalent.



2.2.1.6 Titanium

Kuhn gives an overview on electropolishing of titanium and its alloys [KUHN, 2004]. After him the overall anodic reaction is:



He points out, that titanium tends to build up an oxide layer [KUHN, 2004]. The formation of the titaniumoxide layer follows the equation:



As far as I know it is not investigated whether the reactions given above take place during electropolishing titanium and its alloys using an electrolyte made of sulfamic acid and formamide or not. The conditions for building an oxide layer on the titanium surface in this system are not investigated too. Such an oxide-layer on an electrolytic smoothed and polished surface can be assumed as highly corrosion resistance.

2.2.1.7 Oxygen evolution under transpassive conditions

As described in literature the oxygen formation at the metallic anode takes place by forming $\cdot\text{OH}$ -radicals first [HAM, 1981]. After the classical reaction model adsorption of

hydroxide ions at the metal surface takes place. OH^- anions tend to adsorb at the anode surface. There they can easily react with other species.

Hamann and Vielstich [HAM, 1981] describes the oxygen formation as multi step reaction. The steps in their model are as follows.

In an acid solution the following reaction take place on respectively at the anode. Water splits into protons and $\cdot\text{OH}$ -radicals at first. The radicals adsorb on the surface:



The adsorbed $\cdot\text{OH}$ -radicals react to water and oxygen-radicals.



At least the adsorbed oxygen-radicals form oxygen. The formed gas forms bubbles and descends:



This gives the following overall reaction:



Metal acts as catalyst in this reaction. Taking this in mind the following reactions can be described. Metal and water react to metal-hydroxide, a proton and an electron is split of during this reaction step.



The chemically adsorbed hydroxide reacts to water, metal and oxygen. The oxygen is still adsorbed at the metal surface.

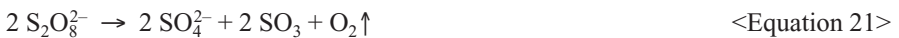


Finally two oxygen atoms combine to oxygen after *<Equation 16>*.

After Gaida oxygen evolution out of sulphate ions is preferred, if the electrolyte has a high content of sulphuric acid [GAI, 2004]. After him two sulphate ions react to persulphate. This is described in *<Equation 20>*:



Persulphate is not stable. It breaks up into sulphate ions, sulphur trioxide and oxygen, see *<Equation 21>*:



Together with water sulphur trioxide reacts to sulphuric acid. See *<Equation 22>*. The acid dissociates into hydronium ions and sulphate ions. This is shown in *<Equation 23>*.



It is still an open question whether the oxygen evolution takes place after one of the mechanisms given above or not [BUHL, 2000]. It can be assumed that metal hydroxide reacts to metal oxide and water. Instead of oxygen evolution passivation takes place. This can be observed at potentials that are higher than the flade potential. Normally potentials higher than the flade potential are used in case of electropolishing. The corresponding reaction would be:



Which reactions take place depends on the electrochemical circumstances. Hamann and Vielstich [HAM, 1981] assume a passivation of the surface as starting point for the oxygen evolution. Buhlert announced a different anode reaction. He assumed that hydroxide (OH^-) loses an electron. In this way a radical ($\cdot\text{OH}$) is formed [BUHL, 2000]:



The radicals ($\cdot\text{OH}$) are very reactive. They join. Water and oxygen is formed. The oxygen forms bubbles and escapes from the electrolytic solution:



Electropolishing is a transpassive electrochemical removal process. The anode potential during electropolishing is highly passive. That is why the hydroxide concentration in front of the anode is supposed to be high. As the OH^- -concentration in front of the anode is high this process can be assumed as possible.

Firstly the oxygen formed dissolved in the electrolyte. After there it is no more oxygen soluble locally gas bubbles build up. These bubbles ascend in the solution after they reach a certain diameter and become stable. The diameter of ascending bubbles depends besides others on the density and the viscosity of the electrolyte and on the surface tension. Bubbles may agglomerate during their ascent. By this way bigger bubbles are formed.

The places or areas where oxygen is formed during transpassive electropolishing are not really known by now. It can be assumed that oxygen is formed at places that are energetically favoured. Such places are lattice defects, roughness peaks or inclusions. This assumption is base on the hypothesis that oxygen is formed in a process with radicals after *<Equation 25>* and *<Equation 26>*.

The other assumption that oxygen is formed from metal hydroxide after *<Equation 19>* is in question. The transition from the chemically to the physically adsorbed state before the recombination of oxygen atoms to O_2 after *<Equation 16>* would require more energy. To say more about this more investigations have to be undertaken.

2.2.2 Cathode reactions

Without cathode the electric circuit is not closed. Without it the electrochemical cell is incomplete. The choice of the right material is necessary. At first the cathode must be resistant against the electropolishing electrolyte. It has to withstand this environment with and without being connected to the electrical circuit.

3 Influence of different manufacturing parameters during electropolishing

3.1 Manufacturing process

An overview over the manufacturing steps is given before the influence of different parameters is explained. *Figure 27* shows the steps of the process of electrolytic brightening, smoothing or deburring respectively electropolishing.

As electropolishing is an electrochemical removal process, it is necessary, that the whole surface to be removed is electric conductive and not isolated by any kind of layer. That is why the metallic workpieces have to be cleaned and degreased before electropolishing. Therefore aqueous solutions of tensides, suds or solvents like isopropanol or acetone are in use. The environmentally mildest cleaning solution should be chosen, that shows the desired results. Often an additionally rinsing after cleaning is not needed. Drying can be necessary to enable mechanical treatment or to prevent contamination of the electrolytes used thereafter for pickling or electropolishing. In any case one has to keep an eye on the electrolytes to prevent contamination or unwanted dilution.

If the cleaned surface cannot be electropolished directly because of rust, oxides or any other layers, chemical or electrochemical pickling can be necessary. If the layers are too thick or the surface is too uneven, grinding, machining or blasting is required. By this mechanical treatment the layers can be removed and the surface can be smoothed as well. The pickling time should be so short, that the layers are just removed and the surface gets not rougher than unavoidable. In general it can be said, that the smoother the surface is before electropolishing the smoother it can be after electropolishing.

The pickling before electropolishing can be done in the same way as in other surface finishing processes [BUHL, 2004h; BUHL, 2004h], see *chapter 3.2.2.2* as well. Chemical and electrochemical pickling techniques are used in industry. Advantageously pickling solutions are used, that contains the same chemicals as the electropolishing electrolyte used.

To avoid unwanted input of chemicals or solvents into the electropolishing electrolyte rinsing might be necessary. Often the rinsing step is done in a cascade. Sometimes additional drying is necessary. In many cases pickling in extra solutions can be avoided. If pickling is necessary, an electrolytic pickling using the electropolishing bath under pickling conditions is possible in many cases. Many metals can be pickled by active anodic removal. Therefore a current density is chosen, that allows active anodic removal. In this case no transport of the workpiece from one electrolyte bath into the other is necessary. The pickling solution cannot be taken into the electropolishing electrolyte, because there is no extra pickling electrolyte. This type of electropolishing process is described in an article [BUHL, 2004h] and is illustrated in *chapter 6.3*.

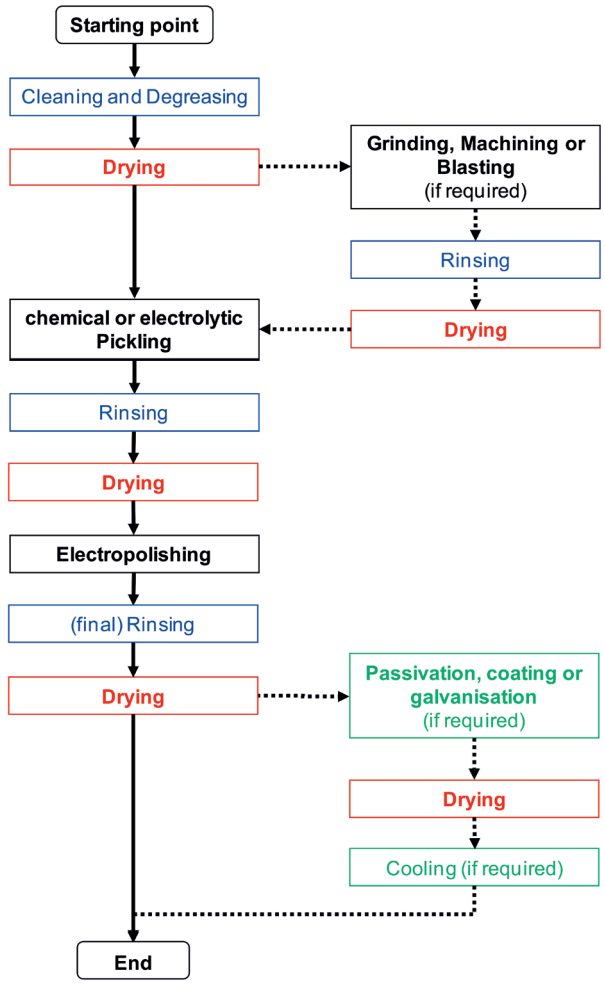


Fig. 27: Process steps of the electropolishing process

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In some cases pickling alone is not enough. If the surface of the metal is too rough, machining, grinding or blasting might be needed before electropolishing. A mechanical treatment is although advantageous, if the surfaces of the different workpieces of a lot differ. For examinations of best electropolishing conditions it is although helpful to equalise the surface conditions by grinding and an additional pickling. During machining or grinding it has to be avoided that abrasive is incorporated into the metal surface. Although abrasive should be eliminated by rinsing before anodic polishing. If necessary, the workpieces have to be dried before electrolytic polishing. Sometimes it is enough to allow the rinsing solution – which is water in most cases – to drain.

After the required pre-treatment is finished, the metallic workpiece can be placed in the electrolyte solution. If the pickling can be done in the electropolishing bath, an additional pickling step is not necessary any more. In most cases the workpiece is placed in the electrolyte without any potential applied. Power is supplied during the placement of the workpiece only in case of metals that are etched in an unwanted way in the electrolyte without an applied potential.

There are different ways to adjust the power. One possibility is to adjust the current wanted at once. In other cases a higher or even lower current is chosen then the current that is required at the end. In this case the change of the current to the desired level is controlled. In most cases the electropolishing process is carried out with nearly constant current density. This means electropolishing is in most cases a galvanostatic process. Although known are electropolishing processes that work with pulsed direct current or with breaks between the electrolytic treatment.

Figure 28 gives a view into an electrochemical cell used for electropolishing sheet metals on an industrial scale. Clearly gas evolution can be seen.



Fig. 28: View into an electropolishing bath used for electrolytic brightening of stainless steel. Reason for foam evolution is oxygen evolution at the anode and hydrogen evolution at the cathode

During the electropolishing process it is necessary to fix the electrolyte temperature within a certain range. Cooling or heating might be required. Only a few electropolishing processes work at room temperature. As current flow through the electrolyte the bath is heated. This has to be taken into account. This heat can be used for processes that work at temperatures above room temperature. The removal should end, after therequired manufacturing result is achieved reliable.

If the electrolyte is used for a longer time or for manufacturing many workpieces, it is necessary to analyse the composition of the electropolishing bath. Water might be evaporated. Electrolyte might be carried out. Metal will be dissolved and water from rinsing before electropolishing might be carried in. This change in composition has to be compensated. If the concentration of metal ions is too high, the electrolyte has to be renewed partly.

After polishing the workpieces are rinsed. Often rinsing cascades are used. They save water. Some of the rinsing solution can be added to the electrolyte to refill the electropolishing solution, if the chemistry allows this. For the final rinsing step deionised water, desalinated or even distilled water is used. Due to final rinsing with this type of water unwanted ions or salts on the metallic surface can be avoided. In some cases it is essential to take care that the electrolyte does not stay for longer times on the surface of the metal. Reason therefore is that some electrolyte solutions attack the metal surface chemically even when no power is applied. If electrolytes attack the surface without power supplied, this can destroy at least the whole manufacturing result. Such a behaviour show some electrolytes used for electropolishingof aluminium, see *chapter 6.5.1*.

The development of water spots during drying should be avoided. On the one hand electropolishing can be the final manufacturing step in metal finishing. On the other hand additional steps may follow. Sometimes electrosmoothing and -deburring is used to prepare a workpiece for galvanisation. In other cases it is necessary to cover the electropolished metal to protect it. Especially if the metal itself is not as corrosion resistant as required, additional covering is needed. Coatings can help to prevent corrosion [BUHL, 2004e; BUHL, 2004f; BUHL, 2004f; BUHL, 2004h]. Therefore transparent powder lacquers can be used. Colouring of the powder enlarges the spectrum of decorative colours that can be used for the finish of the surface, see *chapter 6.3.2* and *Figures 21, 22* and *27*.

3.2 Influence of different process parameters

3.2.1 Classification of the different parameters

In general tree different groups of process parameters can be classified. There are parameters that depend on the system, others depend on the electrolyte and others depend on the material treated by electropolishing, see *Figure 29*. The influence on the manufacturing result and the electropolishing process of different parameters differs more or less. The parameters have to be optimised for an optimal manufacturing result. The different parameters effects the resulting potential at the anode, the development of