

STUDIES AND PERSPECTIVES ON THE TYPES OF CORROSION OCCURRING IN CONTINUOUS CHROMIUM PLATING PLANTS

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Abstract: Corrosion damage to metal materials is often related not only to metal loss but also to the decommissioning of components from the installations, the replacement and installation of which costs about 3% per year of the cost of the material from which they are made.

The effects of galvanic corrosion on the operation of plants and equipment can be anticipated, observed and controlled. Following an economic analysis and the works to be carried out, a balance can be struck between the impact of corrosion of the mechanical elements in the chrome plating bath and the costs for its prevention. The prevention of corrosion at the design stage can lead to lower annual corrosion-related costs, which are much lower than the costs of remedying the causes when the construction of equipment and plants has already been completed.

The aim of this study is based on an analysis of the effect of electrochemical processes in the chromium plating solution on the copper anode bar in continuous chromium plating plants. Initially the forms of corrosion damage to the metal material were identified and then attempts were made to develop methods to reduce and avoid their destruction.

Keywords: galvanic corrosion, chromium plating, electrolytic baths, copper anode bars

1. INTRODUCTION

The use of metal parts in corrosive environments involves coating their metal surfaces with resistant protective coatings. In industrial practice there is a variety of surface coating methods [1,2]. The methods currently applied to prevent and fight against the corrosion of metals depend largely on the shape and size of the object to be protected, the quality of the substrate material, the technological operational parameters of the plant and the possibilities for executing corrosion protection [3,4,5].

Protective coating has the dual role of corrosion protection and increased wear resistance. Chromium plating is a coating process that is achieved by electrochemical deposition of chromium on various metal surfaces. In the case of long bars or pipes that need to be coated with corrosion protection layers, special chromium plating facilities are required.

Chromium plating of long bars in conventional plants with continuous operation is difficult to be performed [6,7,8]. The insertion and removal of bars from electrolyte solutions is difficult, at the top of the tank, requiring complicated lifting devices and large vertical space.

In these cases, continuous chromium plating plants are used for chromium plating of long bars, the operating principle of which is the continuous and controlled

passage of the bars through the chromium plating bath. In these plants the quantity of electrolyte is much smaller, as the bar moves horizontally through the solution [9,10]. The electrochemical phenomena that occur when the bars pass through the solution are different from classical chromium plating where the bar undergoing chromium plating is at rest [11,12,13].

In the present paper, representative forms of corrosion wear of anode copper bars from a continuous chromium plating plant used in industrial enterprises in the area were identified. The design solutions and recommendations for installation and operation that have been used to avoid the destruction of the anode bars, and to minimise the maintenance and repair costs of continuous chromium plating plants will be highlighted [14,15].

1.1 Theoretical consideration. Metal coatings by electrolytic chromium deposition

The electrolytic deposition of chromium occurs at negative cathode potentials and is accompanied by a considerable release of hydrogen. This leads to low current yield values and the presence of pores and cracks in the chromium layer [16,17,18].

Chromium plating baths contain chromic acid as a chromium ion donor and an acid radical called a

catalyst, which favours the cathode deposition of chromium and without which chromium cannot be deposited. Chrome plating baths are made of PVC-coated steel sheet or titanium sheet to ensure high corrosion resistance. Inside the chromium plating bath there are electrical resistors mounted in stainless steel or titanium capsules, which have the role to preheat the electrolyte and bring it to the optimum chromium plating temperature of 65°-70°C [19,20,21].

Chromium plating bath anodes are insoluble and are made of pure lead or an alloy of lead, tin and antimony. The cathode is the steel bar on which the electrochemical deposition of chromium is to take place. The voltage applied to the electrodes of the bath is 6-12 V and the intensity of electric current is up to 24 000 A.

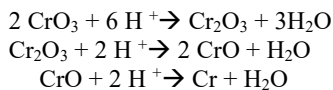
In a chromium plating bath in the operating state there is always a smaller or larger amount of trivalent chromium, which considerably improves the dispersion power of the chromium plating electrolyte but has no appreciable influence on the current yield. When its concentration is increased, the range of the shiny chromium deposits narrows [22].

The main attributes of electrochemically deposited chromium such as hardness, wear resistance, friction, abrasion and corrosion, decorative appearance, etc. have led to its widespread use in a wide variety of industrial fields.

The electrolysis phenomena that occur during chromium deposition are complex and have been the subject of numerous studies and research, with no unambiguous conclusion as to the reaction mechanism.

Briefly they can be presented as follows:

- at the cathode, reduction of hexavalent chromium to trivalent chromium, deposition of metallic chromium and strong release of hydrogen according to the reactions.



- at the anode, oxidation of trivalent chromium to hexavalent chromium concomitant with the release of oxygen.

In order to achieve efficient chromium plating, the ratio of chromic anhydride to sulphuric acid in the electrolyte must be kept constant, optimally 100:1. The current density varies widely between 10 and 100 A/dm² and even up to 200 A/dm². If the current density is higher, the operation time decreases and the yield increases. At current densities lower than 5 A/dm² chromium is no longer deposited at the cathode [23,24,25].

Electrolytic chromium plating differs from other electroplating processes not only in the type of electrolyte but also in the type of deposition obtained.

The very thin layers of chromium (below 0.5 µm) are very thin, only as the thickness of the layers increases (thicknesses between 0.5 and 20 µm), a network of cracks forms inside them. If the thickness exceeds 20 µm, the layers become compact, without pores. Obviously, this behaviour is influenced by the working conditions [26,27].

To carry out the technological process, electric current is fed to the anodes from a rectifier through copper or duralumin bars. The rectifier that provides the anodic attack is a rectifier that works with a current density for the anode attack of max. 50% of the value of the current density required for chromium plating of the bars.

1.2 Description of the plant

The continuous hard chrome plating plant is a plant that works, from the loading to the discharge of the chrome bars, in automatic mode. The kinematic scheme of the chromium plating plant is shown in Figure 1.

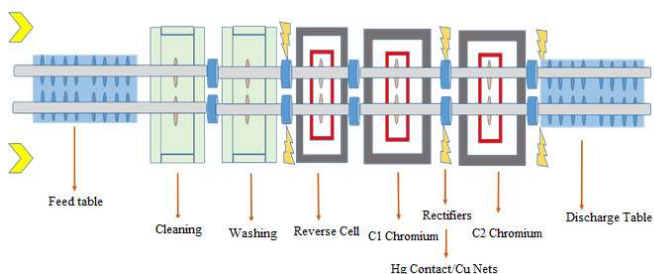


Figure 1. Kinematic scheme of the chromium plating process

The bars are placed on the feed table by hand, where they are automatically loaded on to the supporting rollers by a system of successive steps carried out by pneumatic cylinders [1,2,28]. After loading, an optical system controls the movement of the trolleys which push the bars along the entire chrome plating length, passing successively through the degreasing, washing, anode attack and hard chrome plating cells. At the exit of the last hard chrome plating cell are the bar and bar end detection systems, the feeding and chrome plating cycle continues [29,30]. The bar end detection system detects the end of the bars and controls their discharge from the runways onto the chrome bar discharge bed. The number of chromium plating cells C1, C2 where the electrolysis process and material deposition take place is given by the technological process of progressive deposition of chromium in uniform layers on the bars.

The most serious corrosion-related problems are found in the chromium plating cell where the necessary anodes are found and where the deposition of chromium on the bars take place.

The chromium plating cell consists of a metal tank, equipped with anodes, buffer tank (equipped with feed

pumps, resistance pump, temperature probe, suction filter), vertical pressure pump necessary for continuous mixing of the electrolyte, suction tubing, accessories for temperature control and the minimum and maximum levels of the electrolyte solution, as well as rollers for supporting and guiding the bar.



Figure 2. Electrolytic tank in which chromium plating takes place

Figure 2 shows an overview of the chromium plating cell [1,2,31].

Inside the electrolytic chromium plating tank, circular anodes are mounted equidistantly, through which the cathode-bound bar moves automatically, on which the chromium layer is to be deposited [32]. The anodes are clamped to the copper bar by means of removable bolt-nut assemblies (figure 3). Several groups of contacts are positioned between the basins (these are electrolyte tanks) to ensure the passage of current, thus allowing the deposition process to take place.



Figure 3. Mounting the anodes

The electro-chemical phenomena that occur when the bar passes through the electrolyte solution have a negative influence on the proper functioning of the mechanical systems required for the chromium plating process [33].

As a result of this phenomenon serious problems have been identified in:

- anodes through which the bar to be coated passes during the technological process (figure 4);
- to their clamping system on the electrolytic copper bar (figure 5);
- to the system for the clamping of the copper bars in the supporting bracket (figure 6).

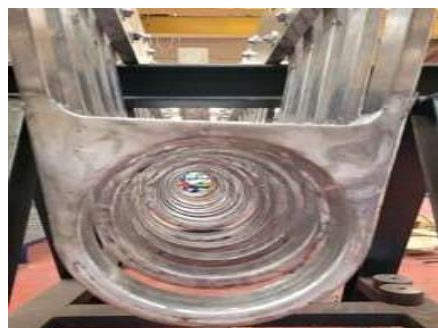


Figure 4. Front-side view of the anode system



Figure 5. How to attach the anodes to the electrolytic copper bar



Figure 6. System for clamping the copper bars in the supporting bracket

1.3 Form of corrosion

In designing the plants and equipment necessary for hard chromium plating and in the case of repairs to these plants, the aspects related to corrosion control and development must be taken into account. Current repairs to a hard chromium plating plant have shown that the anodes and electrolytic copper rods corrode intensively when they are clamped.

An important aspect of the studies is that many types of corrosion damage mechanisms have been found. These mechanisms do not act singularly or independently of each other but in most cases their mode of manifestation is intertwined. It has been found that sometimes corrosion precedes fatigue or acts in conjunction with it, increasing crack propagation rates.

It is obvious that the main form of damage is *chemical corrosion*. During the technological process of chromium plating the chemical reactions taking place in the electrolytic bath, the gases developed, the mechanical impurities, contain substances that occur as a result of random combination in the electrolyte, which leads to corrosion at the level of the anodes. Figure 7 a, b shows such a chemical corrosion of anodes in a hard chromium plating plant.

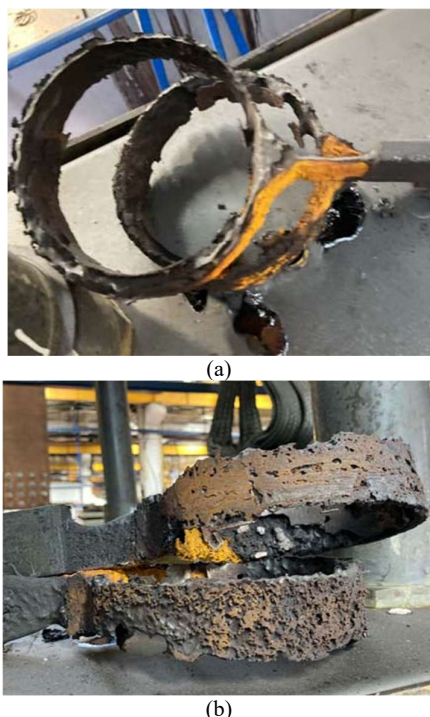


Figure 7. Forms of chemical corrosion of anodes

Figure 8 illustrates the electrochemical deposition that occurs on the anode-rod junction area.

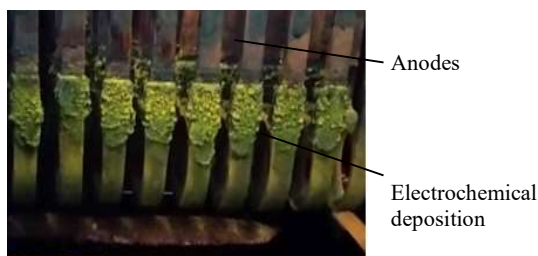


Figure 8. Chemical corrosion of anodes

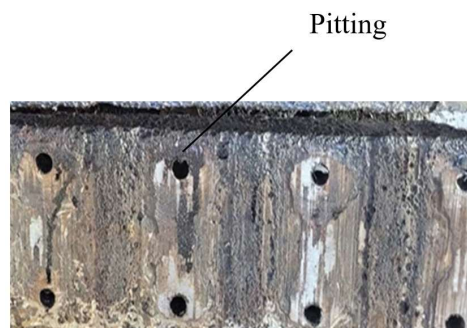
Corrosion products are found to remain on the surface of the material in the form of thick films or films. For this reason, the destruction of the anodes by oxidation does not take place completely because the film formed passivates the surface of the metal material.

The thickness of the oxide layer deposited on the anodes varies very widely, from a few angstroms to millimetre sizes.

It has been found that this film is stable and adheres to the anode surface and thus slows down the corrosion process. The chemical corrosion phenomenon was also found in the case of electrolytic copper bar both in the anode clamping area and in the clamping area between the anode and the anode clamping system. Figure 9 a, b shows the formation of oxides and salts on the electrolytic copper bar.

Another form of corrosion found in both electrolytic copper rods and anode supporting rods is *pitting or spot corrosion*. This is one of the most destructive and intense forms of corrosion and is deemed the most dangerous form of corrosion because it is harder to detect.

The manifestation form is a small area spot that takes the shape of a cavity and has a width to depth ratio of 2/3.



a - anode clamping area



b - electrolytic copper bar clamping area

Figure 9. Formation of oxides and salts in chemical corrosion with pitting corrosion

Figure 10 shows such a corrosion at the anode clamping bar.



Figure 10. Spot corrosion of electrolytic copper bar

Another form of damage to electrolytic, anode-clamping copper bars, similar to pitting corrosion, was *crevice corrosion*, also called concentration cell. The localization of this type of corrosion was found in the areas where the anode rods were clamped to the supporting brackets (Fig. 11, Fig. 12), and cracking of the rod material was also observed in this area.



Figure 11. Copper bar breakage in crevice corrosion



Figure 12. Crevice corrosion

The mechanism of this type of corrosion is similar to galvanic corrosion except that it is generated by differences in the concentration of the medium in contact with a material which can lead to different electrochemical activities. Crevice corrosion is based on poor aeration with the occurrence of anode reaction in this area and cathode reaction on the well-aerated free surface, at the same time the passive oxide film disappears into the crevice.

The anodes are fixed to the electrolytic copper bar by means of clamping bolts. Uncontrolled tightening of the bolts has led to *stress corrosion*. This form of corrosion is considered one of the most dangerous forms of corrosion encountered in practice.

Stress corrosion has manifested itself in inter- or trans-crystalline cracks and even in the breaking of the anode bar.

This was due to the combined action of an aggressive agent and static mechanical stress (elongation) following the tightening of the bolts (figure 13).

In the case of electrolytic copper anode clamping bars, cracking of the material was observed with a breakage of the electrolytic copper bar (figure 14 a, b).

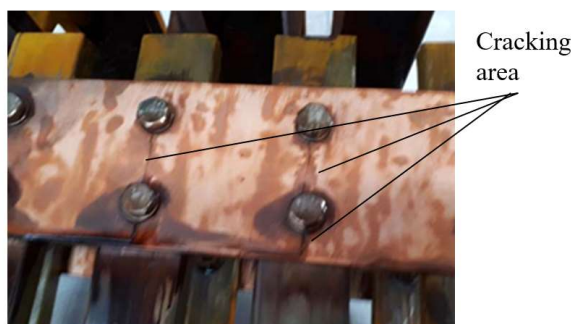


Figure 13. Stress corrosion cracking

The probable cause of this crack, with irreparable damage to the bar, was due to internal stresses occurring in the material, which as a result of chemical reactions during the chromium plating process and external stresses occurring during the clamping on the bracket caused stress corrosion to occur. The stresses required for crack initiation and propagation are usually small, and cracks are more likely to occur due to residual stresses within the material structure.

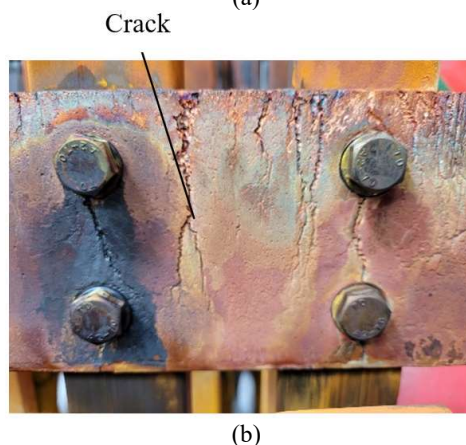
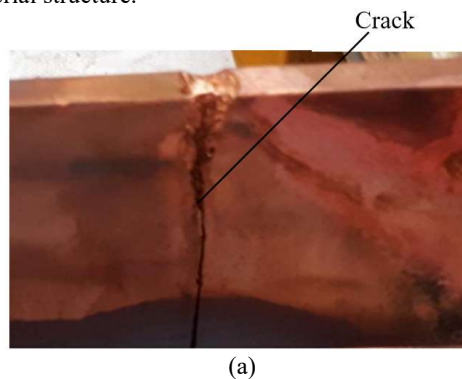


Figure 14 Copper bar cracking in stress corrosion cracking

Studies and analyses carried out during repairs of chromium plating plants have led to the conclusion that the passage of electric current through the anode clamping bolts on the electrolytic copper bars leads to *galvanic corrosion* of the clamping system.

This is due to the different electrochemical potential of the material of the clamping bolts and washers (originally

galvanised steel) between the electrolytic copper bar and the anode rods (figure 15).



Figure 15. Galvanic corrosion of the copper bar

Figure 15 illustrates a strong corrosion in the area of the anode bolt clamping area of the copper bar and figure 16 shows the corrosion of the clamping bolts.

Bolt sheared off due to galvanic corrosion



The trace left by the safety washers upon the assembly of the anode bolts



Figure 16. Galvanic corrosion in the area where the anodes are clamped with bolts



Figure 17. Corrosion of clamping bolts

The effect of internal stresses in the material and external stresses produced by the clamping of various mechanical elements in combination with the corrosive environment can generate fatigue corrosion. Cracks in the electrolytic copper bar are due to the decrease in the strength limit of the material under the action of these two factors. The cyclicity of the process and the corrosive environment cause disturbances to occur in the atomic lattices of the metal after a certain number of cycles, leading to cracks. Crack surfaces caused by fatigue corrosion look similar to those caused by stress corrosion (figure18).



Figure 18. Copper bar breakage due to fatigue corrosion

The defective way of stirring and filtering the electrolyte or the concentration of salts or hydrogen ions in the chromium plating bath leads to residue deposits which, when engaged into the electrolysis process, cause the technological process to be defective and numerous defects to appear on the surface of the bars (figure19).



Figure 19. Defects in chrome plating bars

Figure 20 shows the residues resulting from the chromium plating technological process.



Figure 20. Residues resulting from the chromium plating technological process

1.4 Design solutions adopted

In order to mitigate the effects of corrosion on the studied elements, an analysis of the characteristic factors of the electrochemical process and the action of harmful substances in the electrolyte on the cathode layer was carried out. For this purpose an analysis was made on [1,2]:

- current density;
- how to stir the electrolyte;
- how to filter the electrolyte;
 - temperature of the electrolyte;
 - concentration of salts;

- concentration of hydrogen ions;
- periodic reversal of current direction.

In order to avoid galvanic corrosion the design measures adopted were:

- replacement of galvanised steel bolts, nuts and washers with similar titanium ones;
- for better electrical contact it was decided to replace the copper bars as follows: for lead/tin/antimony alloy anodes duralumin bars will be used and for titanium anodes copper or tinned copper bars will be used;
- controlled tightening of the threaded assembly, using a torque wrench, so as not to create unnecessarily high tightening tensions.

To avoid chemical corrosion the design measures adopted were:

- replacement of the filter pump with a higher power one in order to improve suction and circulation of the electrolyte solution to avoid oxide deposits on the surface of the bar.

In order to avoid spot corrosion and its effects, it was decided to control weekly the value of aggressive polyatomic SO_4^{2-} sulphate anions responsible for this type of corrosion.

In order to improve the behaviour of the anode clamping bar, it was decided to purchase anodes obtained by a die casting process, abandoning anodes obtained by free casting them in moulds.

In order to avoid internal stresses arising from the machining of the bolt mounting holes, the bolts were machined by water jet cutting.

II. CONCLUSIONS

This paper presents an accumulation of scientific information obtained during many years of teaching and research in the field of electrochemistry, corrosion and corrosion protection. The study sought to identify the types of corrosion underlying the deterioration of the copper anode bar and anode connecting elements in the continuous chromium plating plant. By identifying the causes of corrosion of these elements, solutions were sought to remedy and improve the operation of the electrolytic continuous chromium plating process. The solutions adopted minimised maintenance and repair costs.

Careful and continuous monitoring of current density, electrolyte composition and temperature was one of the main objectives. In this way, remarkable changes in the corrosion problem were observed, but also better current efficiency and therefore savings in electricity consumption.

In order to have a better circulation of the electrolyte solution, with intense stirring, the filter pumps were replaced with ones of higher capacity. The better filtration resulted in better retention of mechanical impurities or residual particles in the solution.

Replacing free-cast anodes with die-cast anodes has proven to be a beneficial solution.

Replacing the (galvanised steel) anode bolts and washers on the electrolytic copper bar with a titanium material has proven to be a beneficial solution to avoid corrosion. For better electrical contact, changes were made to the copper bar material as follows: lead/tin/antimony alloy anodes were replaced with duralumin bars and titanium anodes were replaced with copper or tinned copper bars. Depending on the technological process, an adjustable ventilation system has been adopted for better ventilation of the gases from the electrolysis process.

As a result of the solutions adopted, a 25% reduction in the planned maintenance costs of the continuous chromium plating plant was achieved.

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