THE ROLE OF TITANIUM IN ANODIZING AND ELECTROPLATING

Dr.-Ing. Klaus Rüdinger
Managing Director, Technical
Contimet GmbH
Krefeld, Germany

Introduction

The suitability of materials for electroplating is determined by their corrosion-chemical behaviour in conjunction with their mechanical and some of their physical properties. In many cases the existing corrosion problems can be overcome by plastics. But the application of plastics is prohibited where metallic properties are required, such as high mechanical strength and good electric conductivity. One of the materials which therefore are used for electroplating is titanium, since apart from satisfactory mechanical and physical properties it shows a good corrosion-chemical behaviour in many electroplating baths.

Chemical composition and tensile properties

The electroplating industry nearly exclusively uses titanium in its unalloyed form. Commercially pure titanium fully meets the requirements posed by this branch, as regards a favourable corrosion behaviour, high strength, satisfying electric conductivity and easy cold-workability.

Among the commercially pure titanium grades showing similar chemical compositions and meeting the variety of requirements posed by the chemical and electroplating industry, the softer grades are preferred for electroplating (see Table I).

Table I. Mechanical Properties of Commercially Pure Titanium

Grade DIN-No.	UTS kp/mm^2	0.2 YS[+] kp/mm^2	EL.[+] %	RA[+] %
3.7025	30-42	20	30	35
3.7035	40-55	28	22	30
3.7055	47-60	36	18	30
3.7065	55-75	45	16	30

[+] Guaranteed RT Minimum.

They show excellent cold-working properties. Up to a tensile strength of 42 kp/mm^2 they are favored for heat exchanger tubes, as a coating metal for corrosion-stressed troughs and tanks, and as an expanded metal for anode baskets. Commercially pure titanium having a tensile strength of 40-55 kp/mm^2 also permits an application for stressed components working in service temperatures up to about 300°C. It is the titanium grade most frequently used for electroplating applications in the form of heat exchanger tubes, wire, sheet strip, support bars and contacts.

While commercially pure titanium having a tensile strength of 47-60 kp/mm^2 is nearly exclusively used for the construction of pressure vessels, the material preferred by manufacturers for pumps and valves is the hardest grade showing 55-75 kp/mm^2. Higher tensile strengths than possible in the annealed condition are achieved by work hardening, especially of wire. As shown in Figure 1, tensile values up to 100 kp/mm^2 are reached, depending on the titanium grade and on the degree of deformation. Work-hardened wire still showing elongations of about 8-20 % has better spring qualities than annealed wire. This is taken advantages of by using this titanium type for contacts or in form of coils in suspension racks for anodic oxidation of aluminum. For cold-rolled strips, which are also used for contacts, the spring quality is already sufficient in the annealed condition.

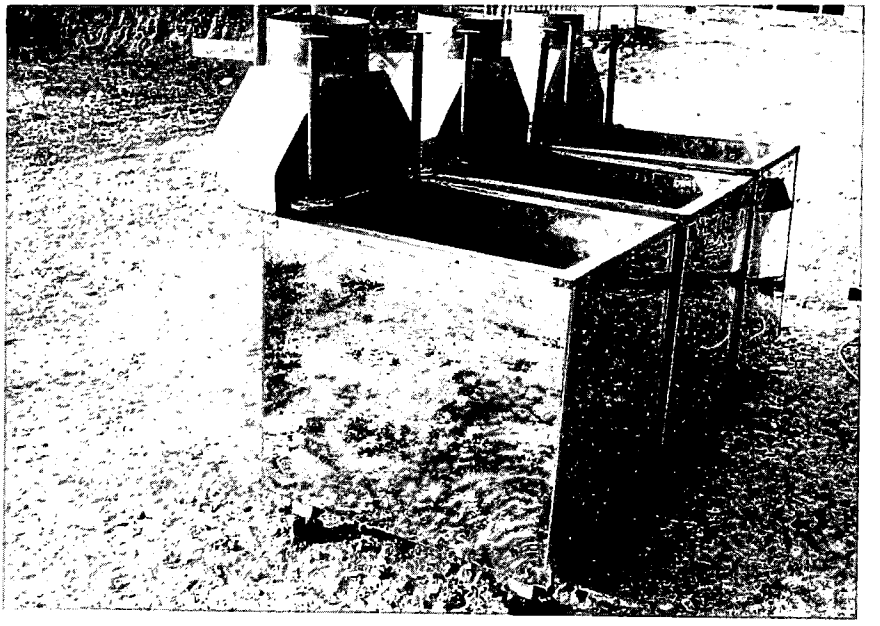


Fig. 1. Titanium tanks for a hand line tin chloride bath. Courtesy: Gebr. Denu, Nufringen.

Physical properties

Among the various physical properties shown in Table II for room temperature (20°C), the density is worth special notice. With 4.5 g/cm^3 it is by 60 % higher than that of aluminum, but those of copper and brass, materials also used for electroplating, are twice as heavy while the weight of lead is 2.5 times that of titanium.

Table II. Physical Properties[1] of Commercially Pure Titanium

Grade DIN-No.	Mean Coeff. of Therm. Expansion[2] per deg. °C. 10^{-6}	Specific Heat cal/g°C	Thermal Conductivity cal/cm. s°C	Electrical Conductivity m/Ωmm^2
3.7025	8.8	0.124	0.054	2.12
3.7035	8.8	0.125	0.054	2.08
3.7055	8.8	0.125	0.054	1.92
3.7065	8.8	0.129	0.049	1.82

[1] at 20°C [2] between 20 and 200°C

The thermal conductivity of titanium being about 0.054 cal/cm x sec. x °C is comparable to that of lead but 10 times lower than the conductivity of aluminum or copper. However experience, also in other industrial branches, has shown that not merely the heat conductivity of the material but the rate of heat transfer is of decisive importance. In view of the low tendency to form instructions on the surface, which can reduce the best transfer quite substantially, titanium often provides advantages.

The electrical behaviour, i.e. electric resistivity or conductivity, of a material is of special importance to electroplating. The specific resistivities for the various c.p. titanium grades range between 0.47 and 0.55 ohms x mm^2/m. It is in fact below that of stainless steel but approximately 20 times higher than that of aluminum. This should be taken into account for the calculation of cross sections of "life" components made of titanium. In case of insufficiently dimensioned cross sections there will be danger of undesired heat increase in current-bearing parts which e.g. on anodizing racks and contacts made of titanium could lead to severe scalds on the aluminum parts to be electroplated. Roughly spoken, current-bearing titanium cross sections can operate outside of the electrolytic bath at a current density of 1.0-1.5 amp./mm^2 in a temperature range between 20 and 80°C and in the electrolytic bath up to 5 amp./mm^2. If higher current densities are required it will be advisable to use aluminum or copper

bars coated with titanium. This combination enables the high corrosion resistance of titanium to be utilized in conjunction with the good electric conductivity of the core metals aluminum and copper.

Corrosion resistance

With an electronegative potential of -1.75 volts titanium's place in the electrochemical series is between magnesium and aluminum (1). Titanium receives its corrosion resistance by a deposition of a passivating oxygen skin on its surface, just like aluminum or stainless steel. Accordingly, a good corrosion behaviour may be expected under neutral or oxidizing conditions, whereas a severely reducing environment causes a breakdown of the passive skin and an attack to the metal. Such conditions are enhanced by hydrofluoric acid, hydrochloric acid, sulphuric acid, oxalic acid and unaerated formic acid (2).

Any exposure to oxygen or air increases the stability of the passive skin. The same effect is initiated by additions of nitric acid, chromic acid and inhibitors like Cu(II)-ions, Fe(III)-ions or Ti(IV)-ions. A thin but dense surface film improving the corrosion resistance in reducing media is also formed by anodized titanium.

In nitric acid titanium exhibits outstanding corrosion properties. The corrosion behaviour of titanium in chromic acid and phosphoric acid at room temperature is characterised by a large passive range extending to a concentration level of 35 %. Under these circumstances the annual material loss in phosphoric acid is not higher than 0.02 mm. Higher temperatures, particularly in case of phosphoric acid, lead to material losses up to 0.1 mm/year maximum.

The corrosion behaviour of titanium in pure hydrochloric acid and sulphuric acid at room temperature is satisfactory only up to a concentration of about 5 %. Slightly higher temperatures lead to an increased corrosion attack which makes an application out of question. An addition of oxidizing substances, e.g. $CuSO_4$, $HCrO_4$, HNO_3 and $FeCl_3$, already by less than 1 % improves the resistance of titanium to reducing media considerably. These inhibitors are often present in operational environments, for process-technological reasons, influencing the resistance of titanium favorably.

Titanium is not resistant to hydrofluoric acid and its salts and thus cannot be applied to such purposes. In most acids, like acetic acid, titanium is not attacked. However, oxalic acid - even when diluted - above room temperature subjects titanium to a severe material loss. Titanium is largely resistant to chlorides, salts and aqueous hydroxides.

An improved corrosion resistance compared to commercially pure titanium under reducing conditions, the other properties being on a similar level, is reached by adding 0.15 % palladium (3, 4). Nevertheless this titanium alloy has not yet been introduced to electroplating.

All of the aforementioned information are related to the corrosion properties of titanium in a currentless condition and exposed to pure agents. They are only to a limited extent informative for their applicability to electroplating. Thus, the behaviour of titanium during electrolysis, especially when anodically polarized, and in the baths used for electroplating is of special practical significance. By anodic polarisation titanium is given an additional corrosion protection becoming effective after the bath voltage has reached 1 V. As in general the bath voltages during electroplating are considerably higher than 1 V, an increased corrosion resistance and a widened spectrum of applications for titanium is a necessary consequence. Using titanium for cathodes often leads to a reduced service life since the hydrogen released at the cathode with rising bath temperatures and after prolonged service periods diffuses into the titanium and causes embrittlement. Similarly leakage currents or shunts could be the cause for an aggravated corrosion of titanium parts. For this reason parts of titanium suspended in an electrolyte in a currentless state are, from time to time, charged with a minor anodic voltage to improve their corrosion resistance.

Experiences until now have shown that in alkaline baths independent on the content of cyanide, in which degreasing is performed by immersion, digesting or electrolytical procedures, and in most of the descaling baths titanium is resistant in a currentless as well as in an anodically polarised state. As expected, titanium is entirely resistant in nitric acid baths.

Titanium exhibits an excellent corrosion behaviour in sulphuric acid direct current baths, as used for anodic oxidation of aluminum. Corrosion tests showed an annual material loss during anodisation between 0.00079 and 0.206 mm, whereas oxalic acids for that purposes attacked titanium severely.

The baths used for electrolytic polishing of metals are usually composed of very acidic electrolytes and operate at high current densities. Depending on their composition, more or less severe material losses were determined in mixed baths of chromic acid, sulphuric/chromic acids, sulphuric/phosphoric/chromic acids or sulphuric/chromic/nitric acids. However, according to experience the material loss due to corrosion is minimized under current load and in the presence of a second metal, e. g. the metal to be burnished. In this case corrosion tests in advance are recommended. Generally, a more pronounced material loss due to corrosion must be feared in baths containing compositions of fluorine. Titanium can be used in aqueous solutions of hydrofluoric acid, if the bath belongs to an anodic cycle. But in such cases the anodizing racks of titanium will suffer a reduction of service life.

Recently, titanium has proved to be resistant even to fluorine-ions in a burnished chromium-plating bath (5). During currentless tests no material loss but just a slight darkening occurred at temperatures of 50°C. When charged with a cathodic current of 25 amps./dm^2 and a temperature of 54°C no material was removed due to corrosion, either. In polishing baths, which consist of sulphuric and/or phosphoric acids titanium normally is resistant.

Hard-chromium plating baths consisting of chromic acid and sulphuric acid just lead to minor material losses of less than 0.01 mm/year both in a currentless and in an anodically polarized state. But hard-chromium plating baths containing fluorine, e. g. the SRHS-bath, throw severe attacks to titanium and make an application impossible. Material losses up to 30 mm/year are expected in this case.

Good corrosion resistance is observed in nickel-plating baths, based in their chemical composition on nickel sulphate, nickel chloride and boron acid and also corresponding to the Watt's type, regardless whether charged with current or not. Just as in nickel baths the behaviour of titanium is considered good also in cadmium, brass, silver, rhodium, gold, platinum and copper sulphate cyanide baths with or without a current load, as well as in tin chloride bathes, Figure 1.

Application

In view of its mechanical, physical and process-technological properties and of its corrosion behaviour, titanium can be utilized successfully and minimizing costs for electroplating even when taking economical considerations into account. Some of the characteristic applications of titanium in the surface finishing industry will be elaborated on, hereafter.

Titanium for suspension racks in anodic oxidation of aluminum

Of particular significance are processes to oxidize aluminum anodically using direct current and sulphuric acid as an electrolyte. The concentration of sulphuric acid is about 20 %, the operating temperature between 20 and 80 °C, the voltage at 20 V and the current density, depending on the desired type of oxide coating, between 0. 6 and 2. 8 amps. /dm^2.

Other processes using oxalic acid electrolytes and operating with d. c. or a. c., as well as the Benough-Stuart-process with chromic acid as electrolyte, are of minor importance.

Common for all processes is the aluminum workpiece being connected to the anode, immersed in the electrolyte, and oxygen being released at the anode upon the action of electric current. The oxygen is combined with aluminum on the workpiece' s surface to form aluminum oxide providing an improved surface protection. A current-loaded suspension rack immersed in the electrolyte and carrying the aluminum workpiece to be plated, clamped between contacts, functions as the anode.

In conventional designs these suspension racks including the contacts also consist of aluminum. But this causes an anodic oxidation also of the suspension rack during electroplating of the workpiece, obstructing the energy transfer at the contact points. Therefore aluminum suspension racks have to be pickled in caustic soda following each anodic treatment, in order to remove the oxide film. Since aluminum is not resistant to caustic soda, each pickling operation means a certain material removal from the rack and a reduction of the cross section. The contacts will lose their acute edges and the rivets will get loose. This steady wear is the cause for repetitive repairs of the locations of suspension. The average service life of racks in current use is only a few weeks until they have to be exchanged against new ones.

Numerous experiences have shown that titanium exhibits a satisfactory resistance mainly to sulphuric acid baths as are preferred for anodic oxidation, while it is attacked by oxalic acid agents. Phenomena of an adverse effect to the material do not occur during degreasing, dyeing and densifying of the workpieces, either. Pickling in caustic soda solution is not necessary when using titanium. Only for subsequent burnishing of the workpiece it should be considered that titanium is generally not resistant to burnishing baths containing fluorine-ions, and therefore can be used for this purpose to a limited extent only. Racks made of titanium are not suitable either for eloxal processes with a. c. supply by conventional procedures.

There are two possibilities to use titanium in most of the bath combinations for anodic oxidation of aluminum. Firstly the common suspension racks remain being made of aluminum but the contact consist of titanium; and secondly, both suspension racks and contacts are entirely made of titanium.

Figure 2 shows anodizing racks completely manufactured of titanium. This is the most favorable solution since the proneness to repair is minimized, and service life as well as operational security are much better than in the case of aluminum racks. This results in a labor economy both in terms of time and, last but not least, of operators. Apart from this, titanium racks are of advantage were burnishing additions are used which attack racks coated with plastics.

If only titanium contacts are used, as shown in Figure 3, it becomes necessary to protect the joints at the aluminum racks from contact corrosion, that means the complete rack must be coated with rubber or plastics, as it has been common practice till now. But this raises a danger of detachment of the plastics coating at the joints, permitting the bath agent coming into contact with the rack and slowly destructing the metal. However both applications have proved their qualification depending on the kind of stress and operation.

For suspension racks of titanium the same design and manufacturing processes can be used as for aluminum racks. However, the higher tensile strength and lower electric conductivity of titanium compared to aluminum should be considered during designing. Compared to aluminum, the electric conductivity of titanium has hardly any influence on the anodic oxidation itself, because the rack does not need to be overdimensioned to compen-

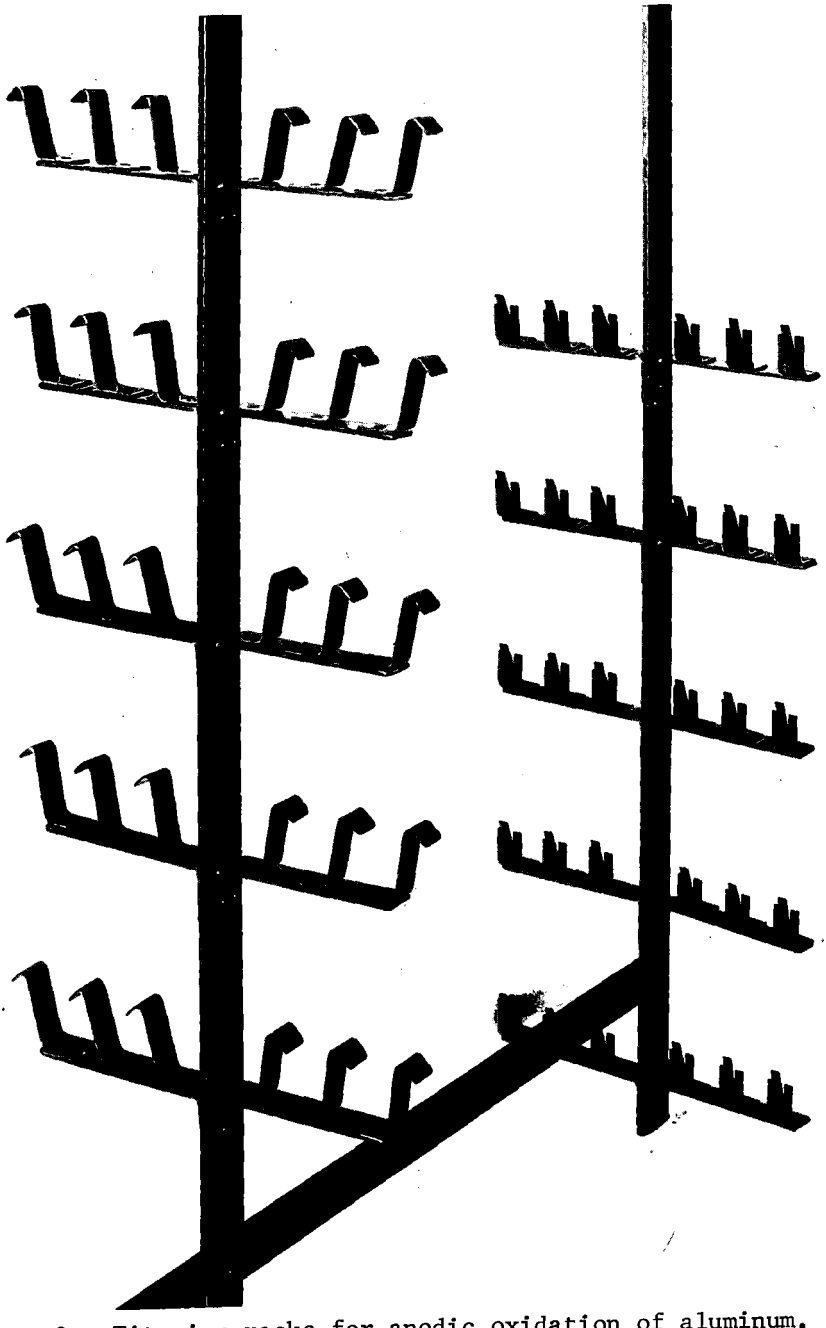


Fig. 2. Titanium racks for anodic oxidation of aluminum.

sate for a material loss due to corrosion, as is the case with aluminum. The current density, ranging about 1.8 amps./dm^2, is not very high either. As stated before, the electric conductivity of titanium permits a current load of 1.0 amps./mm^2 to be charged on the rack cross section at a bath temperature of 20°C, and 1.5 amps./mm^2 for 80°C. If a higher current load is required, necessitating an undue increase in cross section for titanium and an uneconomical application, it is possible to coat copper or aluminum sections with titanium. Hereby the high electric conductivity of the core metal can be combined with the good corrosion resistance of titanium.

Larger metal cross sections must inevitably be selected if anodic oxidation is followed by electrolytical burnishing requiring higher current densities. A too small cross section at the contacts will lead to a heat localisation causing spots of arcing, undesirable discoloration or decomposition of the burnishing bath. Therefore, a good contact with the metal to be plated should always be taken care of, in order to properly utilise the rack metal and cross section.

All commercially pure titanium grades are suitable materials for suspension racks and contacts. They differ from each other to a remarkable extent only in their tensile strength and cold workability whereas their corrosion behaviour remaine unchanged. As far as contacts are used consisting of wire, unalloyed titanium in both of the lower strength qualities are of particular suitability. Their average tensile strength in soft-annealed condition is below 50 kp/mm^2 and in work hardened condition up to 85 kp/mm^2 whereby a higher spring tension is combined with still acceptable toughness properties and good deformability.

A cost comparisonbetween suspension racks of aluminum and of titanium at first shows that the purchase price of a pure aluminum rack is lower than of an aluminum rack equipped with titanium contacts, or a rack entirely made of titanium. On the other hand, a titanium rack has a practically unlimited service life. It easily lasts 30 times as long as a rack of aluminum and sometimes exceeds this limit by more than twice as much. This advantage, combined with lower repair costs than in the case of aluminum and with an elimination of pickling, is in favor of titanium-equipped racks after a service period of 4-5 weeks, and of a pure titanium rack, according to a very careful estimation, already after 2-3 months. This does not take into account that, when changing over to titanium racks, working practically free from

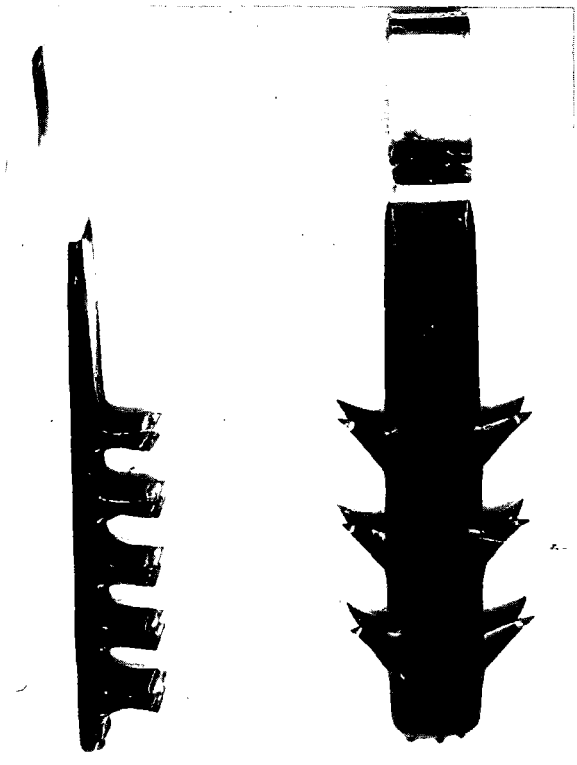


Fig. 3. Plastic coated aluminum racks with titanium contacts for anodic oxidation of aluminum. Courtesy: M. Esser, Solingen.



Fig. 4. Titanium anode baskets for electroplating baths.

any maintenance, interruptions of operation and the amount of rejections will be further minimized.

Titanium for anode hooks and baskets

Electrodeposition of nickel is primarily done in sulphuric acid baths. The additions used are boric acid, chlorides (mainly nickel chloride and sodium chloride), burnishing and wetting agents as well as conducting salts. Chloride and sulphamate baths serve for hard-plating of nickel. Apart from nickel baths, anode hooks and baskets of titanium are also used in copper baths, acidic zinc baths and other electrolytes, with great success and economy.

The anodes used are cast, rolled, or consist of plates fastened to wires and suspended in the bath parallel to the goods to be electroplated. Another type of suspension that has gained importance in the past few years and that offers considerable advantages over wires is the application of anode hooks of titanium. Titanium anode hooks provide a larger contact area and, thus, a higher current transfer. Anode plates can completely be immersed into the bath and used up to a very tiny remainder by applying screwed anode hooks. This means a much better utilisation of the anode material and a considerable reduction of operation costs.

The most significant application field for titanium in nickel-, copper- or zinc-plating is as a material for anode baskets. As shown in Figure 4, anode baskets are cubic containers whose forward and rear walls consist of 0.8-1.0 mm thick expanded metal of various mesh sizes. The cross section of the basket hooks must be so dimensioned that the current density does not exceed 1 amps./mm^2. In general, the basket hooks are manufactured of bars in square or flat cross sections. They shall rest with one edge on the anode bus with a possibly high contact pressure, for the sake of an optimum current transfer from the bus to the basket. A contamination of the baths by anodic mud is prevented by packing the titanium baskets into bags. Suitable bag materials are cotton, flannel, or synthetic fibres like Terylene, PVC, Polypropylene or Nylon. The anode bags shall fit tightly and stiffly around the titanium baskets, especially in baths where the electrolyte is severely agitated and the baskets would flutter around otherwise. The bag shall be exchanged and washed in certain intervals to remove the excessive anode mud which would obstruct them and aggravate the bath resistance.

The savings resulting from an application of titanium anode baskets and from the consequent replacement of expensive metal plate anodes by pellets, granals or even scrap are in the order of 30 %. Further advantages are a constant anode surface, a uniform electric field distribution in the bath and a facilitated replenishment of the anode metal used up by simply refilling of the basket. This is less time-consuming than exchanging the used-up plate anodes against new ones contained in fresh bags. The anode baskets only need to be removed from the bath if they contain too much mud and have to be cleaned.

Titanium coils for chromium-plating baths

Chromium-plating baths mainly consist of aqueous solutions of chromic acid with minor additions, e. g. of sulphuric acid, chromic sulphate, chromic chromate or fluorsilicic acid (about 2. 5 %). They should, therefore, be regarded as strong oxidation agents. The operating temperature is between room temperature and about 65 ^{o}C.

Chromium-plating equipment often consist of steel trays lined with wire-reinforced glass plates or with antimonious lead. In some cases it is possible to use brick-lined trays. The bath can be heated by various methods. One possibility is to place the smaller tray containing the chromium-plating solution in a second larger tray filled with water. Tubular heating coils passed by steam or hot water will effect the heating. The second possibility consists of conducting the heating coils directly through the chromium-plating bath so that the outer water jacket becomes superfluous. Shining chromium coatings are achieved only in a narrowly limited temperature range, depending on the current density. For this reason, it is of special significance to maintain the operating temperature exactly. For continuous service this means that, due to the high amperage, the chromium-plating bath is constantly heated and the coils which firstly were required for heating up can now serve as cooling coils. The tubing for external heating up the water bath are made of steel. Although more favorable, internal heating is difficult because the service life of many conventional materials in a chromium-plating bath is too short. Up till now, these heating and/or cooling coils have been manufactured of lead alloyed with tin or antimony. But these did not show a fully satisfying corrosion behaviour. Apart from the low thermal conductivity of lead the adverse features are aggravated by low strength and high weight. This necessitates very thick-walled tubes and rigid supporting structures for all lead heating coils.

Since titanium is about 2. 5 times lighter than lead but has a much higher tensile strength, heating coils can be produced of titanium much easier, simpler and without any supporting structures. A heating coil of lead of about 45 kg in weight is comparable in its thermal conductivity with a heating coil of titanium weighing about 3 kg only. Their heating surface is by 25 % smaller and the costs for heating with vapor are up to 50 % lower (6). The corrosion resistance of titanium to chromic acid is outstanding in the usual concentration and temperature ranges. Heating coils made of tititanium and exposed to chromium-plating solutions containing 25 % chromic acid do not show the least corrosion stains even after several years of operation.

The materials coming into question for heating coils are the two softer commercially pure titanium grades permitting an easy cold working and welding. Heating coils can, without difficulties, be made of welded tubes because the corrosion properties of titanium welding joints are entirely identical to those of unwelded sheet. Figure 5 shows standard heating and cooling coils of titanium manufactured in the dimensions 25. 4 mm outer dia. x 0. 9 mm wall thickness x 6. 100 mm length having a heating area of about 0. 5 m^2. If a larger heating area is required several standard coils can be connected to each other by rubber or plastics hoses. This arrangement permits an exchange of only the damaged coil, in case of trouble or for repair.

Titanium components like, in this case, heating and cooling coils shall not be placed in the vicinity of parts charged with a positive or negative voltage. Stray current can lead to surprising corrosion phenomens. An increased corrosion loss is avoided by maintaining a distance of about 250 mm, by insulated coil supports or by suspension of glass or plastics shields (7).

Titanium for racks in hot galvanizing baths

To transport goods through hot galvanizing baths you need hooks, frames and racks, manufactured by conventional processes out of iron. But such suspension racks have one disadvantage: just as the goods to be plated they are wetted by liquid zinc and, thus, withdraw zinc from the bath. Therefore suspension racks of steel are to be pickled after each operational step. Every pickling operation entails a material removal from the rack and, thus, a reduction in cross section leading to frequent repairs.



Fig. 5. Standard heating and cooling coils of titanium tubes. Courtesy: H. Meyer, Willich.

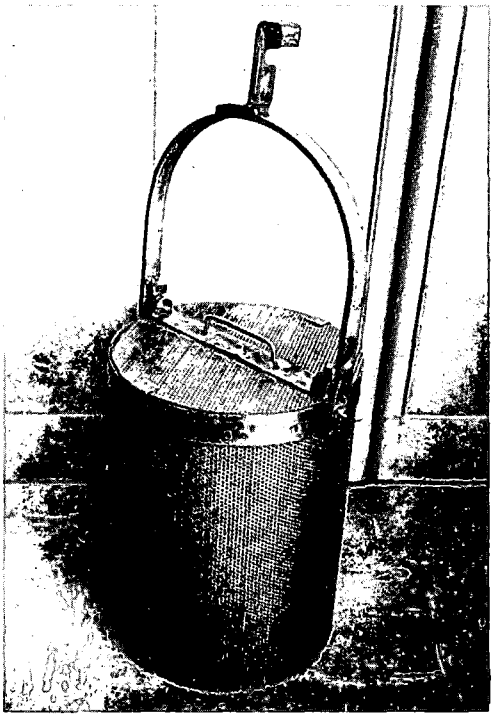


Fig. 6. Titanium pickling basket for galvanizing baths. Courtesy: Gebr. Denu, Nufringen.

Due to their corrosion resistance, strength and low weight all commercially pure titanium grades are suitable for the manufacture of hooks, frames and suspension racks in hot galvanizing baths. Titanium is not attacked by the commonly used pickling solutions free from hydrofluoric acid. Figure 6 illustrates a pickling basket for hot galvanizing of small workpieces. The advantages of using titanium for rack carriers lies in its stability of shape because the acids and fluxes used for hot galvanizing do not attack titanium. Furthermore, titanium does not pick up molten zinc so that no zinc is withdrawn from the bath by the suspension racks. This entails a lowering of pickling agent consumption. Under operating conditions titanium racks have already reached a service life which exceeded that of steel racks by 10 times and more.

Economical considerations reveal that, in spite of the higher expenditures necessary to procure titanium racks, the minimisation in the bearing cross sections, the decrease in corrosion, the avoidance of rack pickling, the higher stability in shape, and the prolonged service life will result in substantial cost savings.

Platinum-plated titanium electrodes

The corrosion resistance of titanium is based on a stable self-curing oxide film on the metal surface which immediately develops in air at normal or elevated temperatures. Titanium remains corrosion resistant as long as this oxide skin is maintained or constantly reproduced. However, this oxide skin, developing also on the metallic bright material, has a very high electric resistivity so that a charge exchange with the electrolyte cannot take place when using titanium for electrodes. But when titanium is costed with platinum, this platinum coating resumes the function of the anode and enables the current flowing easily from the anode to the electrolyte (8). Hereby the platinum-plated titanium anode combine a large number of advantages. It is much cheaper, lighter and stronger than e. g. solid platinum anodes and operates without any sign of dissolution even in case of porous platinum coatings.

Electroplating uses with great success platinum-plated titanium anodes in acidic precious metal baths (rhodium, palladium, gold etc.) as undissolvable anodes (9, 10). For rhodium-plating baths containing sulphuric acid the concentration of sulphuric acid is of striking importance for an economical utilisation of platinum-plated titanium anode. If the concentration of sulphuric acid rises

too abruptly, say by more than 10 %, titanium can be attacked through the pores of the platinum coating. This means that in case of prolonged service interruptions the platinum-plated titanium anodes should either be polarized slightly anodically or removed from the bath.

For a couple of years gold-plating baths have been equipped with undissolvable anodes (11). Significant reasons for using undissolvable anodes are to avoid pollutions of the gold-plating bath by other metals from the gold anodes, and to keep the current output at the anode and cathode possibly on the same level. Depending on the type of gold-plating bath you can use undissolvable anodes of stainless steel, graphite, nickel/chromium alloys or platinum. Platinum-plated titanium anodes have also done an excellent job in anodic gold-plating baths. Here it is essential to meet the requirements of gold producers regarding a high anode/cathode ratio by a specific shaping of the anode but without necessitating too large bath size.

The most significant anode materials for chromium-plating baths are lead and lead alloys. But those lead anodes have two big disadvantages: firstly, the passive skin developing on lead anodes suspended in the bath without any current supply; secondly, the formation of lead chromate entailing a pollution of the bath. Platinum-plated titanium anodes have proved suitable above all in automatic chromium-plating equipment for rotogravure cylinders, where it replaces the conventional lead anodes. Uniform and smooth coatings are obtained without necessitating a repetitive filtering of the bath.

Also the acidic copper sulphate bath is of great importance for the application of platinum-plated titanium anodes. Acidic coppper sulphate baths are chiefly used for applying thick copper coatings. The plating baths mainly consist of copper sulphate, sulphuric acid and certain additions. In the course of time the acidic copper sulphate baths are enriched with copper sulphate because the copper is partly dissolved in a monovalent form at the copper anode and oxidized in the open air. In order to prevent such an enrichment, a part of the copper anodes is replaced by undissolvable anodes of platinum-plated titanium.

The automobile industry inserts platinum-plated titanium anodes in acidic activation baths, e. g. in advance to nickel-plating; platinum-plated titanium hooks are used during electropolishing of small workpieces for suspension hooks in aggressive electrolytes.

Already to-date platinum-plated titanium is a well known anode material for electroplating. Depending on its intended application the anode may be made of wire, bars, sheet or expanded metal of titanium. Additional power supplies from titanium-coated copper bars can be used for very high loads and uniform current distribution. The platinum coating is applied either by electroplating, by thermic or vacuum-technological processes. While platinum is decomposed in the course of service time, titanium will be preserved completely and can be platinum-plated again, if desired. When treated according to specification the platinum-plated titanium anode can reach a service life of 10 years and more, whereby the higher procurement expenditures will be re-gained within a short time.

Conclusion

Among the materials used in electroplating and anodizing titanium shows a variety of advantageous mechanical, physical and corrosion-chemical properties, which minimize process costs and improve process economy. Therefore titanium hooks, racks, coils, baskets, anodes, pumps and containers are frequently used in many anodizing and electroplating baths, for which widen application can be expected.

References

1. Latimer, W. M., "The Oxydation States of the Elements and their Potentials in Aqueous Solutions," New York: Prentice Hall., 1938, pp. 249-252.

2. Rüdinger, K., "Zum Korrosionsverhalten von Titan," Österreichische Chemiker Zeitung, Vol. 64, No. 1, 1963, pp. 7-14.

3. Stern, M. and Bishop, C. R., "The Corrosion Behavier of Titanium-Palladium Alloy," AMS Trans., Vol. 52, 1960, pp. 239-256.

4. Rüdinger, K., "Technologische Eigenschaften und Korrosionsverhalten einer Titanlegierung mit 0,2 % Palladium," Werkstoffe und Korrosion, Vol. 16, No. 2, 1965, pp. 109-115.

5. Rüdinger, K., "Eigenschaften von Titan und seine Anwendung in der Galvanotechnik," Metall, Vol. 24, No. 12, 1970, pp. 1303-1314.

6. Freude, G., "Die vielfältigen Einsatzmöglichkeiten von Titan in der Galvanotechnik," Metalloberfläche, Vol. 24, No. 7, 1970,, pp. 248-251.

7. Weiner, R., "Titan als Werkstoff in der Galvanotechnik," Galvanotechnik, Vol. 53, No. 7, 1962, pp. 322-334.

8. Cotton, I. B., Platinum Metal Review 2, 47 - 7, April 1958.

9. N. N., "Platiniertes Titan - ein neuer Anodenwerkstoff," MR + V, Vol. 17, No. 2, 1968, p. 100.

10. Kühn von Burgsdorff, J. W., Platiniertes Titan als unlöslicher Anodenwerkstoff," Galvanotechnik, Vol. 59, No. 8, 1968, pp. 659-666.

11. Roggendorf, W., "Praktische Galvanotechnik," Eugen G. Leuze Verlag, Saulgau, 1. Auflage 1958, p. 285.