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METHOD OF ELECTROCHEMICAL RECOVERY OF WASTE WATER AND ELECTROLESS COPPER PLATING ELECTROLYTE

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ЭЛЕКТРОХИМИЧЕСКАЯ РЕГЕНЕРАЦИЯ ЭЛЕКТРОЛИТА И СТОЧНЫХ ВОД КОНТАКТНОГО МЕДНЕНИЯ

Summary. The process of contact copper plating electrolyte regeneration using ion-exchange membranes is studied. The high efficiency of the process and the possibility of organizing a closed cycle are shown. The calculation of the energy consumption of the method was made. It is shown that the energy consumption for the regeneration of the etching solution is 400 kW·h/m^3 (20 Euro/m^3) and for the regeneration of the copper plating solution is 600 kW·h/m^3 (20 Euro/m^3). The applicability of the proposed method for the wastewater recovery process after the contact copper plating process is also shown.

Аннотация. Исследован процесс регенерации электролита контактного меднения с использованием ионообменных мембран. Показана высокая эффективность процесса и возможность организации замкнутого цикла. Произведен расчет энергозатратности метода. Показаны энергозатраты на регенерацию раствора травления составляют 400 кВт·ч/м^3 (20 Евро/м^3) а на регенерацию раствора меднения 600 кВт·ч/м^3 (20 Евро/м^3). Также показана применимость предложенного способа для процесса регенерации сточных вод после процесса контактного меднения.

Key words: contact copper plating, filler wire, copper concentration, ion-exchange membrane, membrane electrolysis.

Ключевые слова: контактное меднение, присадочный провод, концентрация меди, ионообменная мембрана, мембранный электролиз.

1. Introduction

Welding wire is used as a consumable for semi-automatic welding. To obtain copper-plated wire, the contact coating method is used. To do this, the steel wire is immersed in an acidified copper sulfate solution. Here, as a result of the difference in electrode potentials, a cementation reaction occurs: an iron ion goes into solution and copper deposits on the surface of the wire. After this, the wire is passed through a dragging, which compress the copper coating. As a result, its surface becomes glossy, acquiring a characteristic pink color.

The thickness of the final coating is 6 μm. The total copper content in the steel wire, according to GOST 2246-70, should not exceed 0.25%. European standard DIN 8559 allows an increase of this indicator to 0.30%. If the welding wire contains a larger amount of copper, then the welds formed with its help are characterized by reduced resistance to cracking and impact strength.

Copper-coated wire has an aesthetic appearance, but is not appreciated for this. One of its main characteristics is a low contact resistance, which means a better current supply. According to this indicator, copper-plated wire differs from the standard analogue coated with technological lubricant by about 100 times. Low contact resistance, in addition to stable arc burning, causes weak spatter of the electrode metal during welding.

The surface condition has a direct effect on the uniformity of the wire feed and the force required for this. For example, a wire without a copper coating is characterized by an unstable supply, high abrasive wear of the current-carrying tip and grabbing to the inner surface of its channel. In this process grease is the reason for the increase in the number of such tacks. Copper-coated wire requires less force to push through and does not contribute to the rapid wear of the tip channel. It is supplied in coils or cassettes and in the form of an ordered and tight ordinal winding. This ensures the continuity and uniformity of its flow.

Another undoubted advantage of copper-plated wire is the minimum amount of impurities harmful to the weld. Its copper-free counterpart is an active supplier of hydrogen. The culprit of this situation is the same technological lubricant. It contains fatty acids, alkalis and water. In addition, it is capable of adsorbing moisture from the air. As a result, the process of wire corrosion is accelerated, and hydrogen gets into the seams, causing their porosity.

Copper-coated wire reduces the time from the first touch of the metal surface to stable burning of the arc by 2-3 times in comparison with non-copper. It promotes the formation of symmetrical and uniformly sized metal droplets at the end of the electrode and their uniform transfer to the weld pool. As a result, the quality of the seams is improved, and spraying is reduced approximately by 40%.

In addition, it should be noted that due to the copper coating, it is possible to improve the characteristics of welds. Their resistance to rupture or shock loads increases, their ability to tolerate temperature changes improves, and the number of defects decreases. In addition, due to the smooth coating, the wire feed speed and labor productivity is also increased.

The raw material for contact copper plating is welding wire with diameter of 1.20-2.0 mm according GOST 2246-70 from low carbon steel grade Sv-08G2S and others.

The technological scheme of wire copper plating at the installation of high-speed chemical copper plating consist of the following stages:

- wire unwinding;
- degreasing;
- hot water rinsing;
- cold water rinsing;
- acid etching;
- copper plating;
- cold water rinsing;
- dragging and greasing;
- winding and packing;

The installation is designed for high-speed (up to 5 m/s) copper plating of low-carbon and alloyed welding wire with a diameter of 0.8-2.0mm per thread (1 thread) with calibration.

Unwinding and winding of copper-plated wire is made from a 1 t coil to a 0.5 t coil. Processing of wire at the installation takes place sequentially in solutions of hot degreasing, etching in sulfuric acid, contact copper plating in an acidified solution of copper sulfate, rinsing and in a liquid lubricant dragged through a fiber.

To immerse the wire in technological solutions the installation of roller systems are used that allow you to vary the processing time of the workpiece. To obtain a high-quality copper coating with a thickness of 0.15-0.50 μm at a pulling speed of 4 m/s, it is necessary to use a workpiece with a quality of residual process lubricant on the surface of not more than 0.5 g/m², an increase the amount of technological lubricant on the surface of the wire leads to a decrease in processing speeds and deterioration of the quality of the coating.

The working conditions of the main stages are following:

- degreasing alkali solution at 60-80 ^{0}C;
- etching solution H_2SO_4 (160-220 g/l), $FeSO_4$ (<80 g/l);
- copper plating solution $CuSO_4$ (160-220 g/l), H_2SO_4 (60-100 g/l).

Due to etching process

$$Fe + H_2SO_4 = FeSO_4 + H_2 \quad (1)$$

iron concentration in eatching bath is encreasing from 0 g/l in a new bath up to 80 g/l and then iron sulphate start to crystallyze in acide solution. Also sulfuric acid concenrtation decreases and etching bath must be changed.

In copper plating solution copper concentration decreases and iron concentration increases due to cementation reaction

$$Fe + CuSO_4 = FeSO_4 + Cu. \quad (2)$$

At low copper concentration the copper plating process became too slow and solution must be chanched.

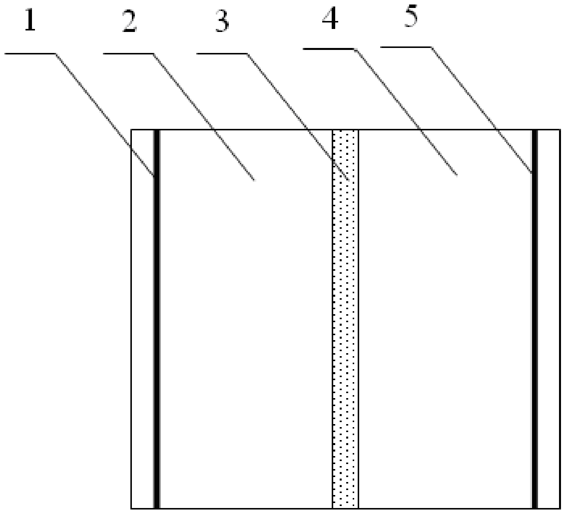
Due to abovementioned reaction (1) and (2) there are huge amount of solutions containing sulfuric acid, copper and iron sulphates are formed on factories which produses copper plated welding wire.

The most used method for such waste is neutralisation by calcium hydroxide. with formation. Such method is relatively cheap but the disadvatage is formation of copper and iron hyrohide mixture and cacium sulphate precipitate which hard to reuse and only water after precipitate fitration can be reused.

The aim of present investigation was usage of membrane electrolysis for regeneration of etching and plating solution for welding wire plating.

2. Experimental

The waste etching and copper plating solution from welding wire plant was used for laboratory tests. The experimental membrane electrolyzer was made from 5 mm sheets and consists of 2 cells, 1 dm^3 each. They were combined through anionic exchange membrane MA-40 (Fig. 1).



1 – cathode (stainless steel); 2 – cathode cell; 3 – anionic membrane MA-40; 4 – anode cell; 5 – anode (lead).
Fig. 1 – Scheme of laboratory setup.

The concentration of sulfuric acid in initial and obtained solution was determined by acide - alkaly titration and concentration of iron and copper ions by complexometric titration according to OST 107.460092.01-86.

3. Results and discussions

The initial concentration of sulfuric acid in obtaining etching solution was estimated as 100 g/l and iron sulphate concentration was 82 g/l. The cathode cell 2 (Fig. 1) was fill by such solution; anode cell was fill by sulphuric acid (120 g/l). At a constant current of 8 A during 7 hours (cell voltage varies from 4 to 6 V), the concentration of sulphuric acid in anode cell reached 200 g/l and can be used in etching bath.

The cathode solution can be diluted twice with sulfuric acid addition or electrolysis continued to pH rising over 3, and iron hydroxide formation

$$Fe^{3+} + 3OH^{-} = Fe(OH)_3. \quad (3)$$

The iron hydroxide precipitate can be filtered, dried and used as pigment [1] or as raw material for steel production.

The waste solution from copper plating bath contain $CuSO_4$ (110 g/l), H_2SO_4 (30 g/l) and $FeSO_4$ (105 g/l), anode cell was fill by sulphuric acid (120 g/l).

After 7 hours of electrolysis at 8 A the copper sulphate concentration decreases up to 1 g/l and iron hydroxide precipitate formed in anode cell the sulfuric acid (200 g/l) was formed as in case of etching solution recovering. Stainless steel cathode was weighted before and after electrolysis and the weight of deposited copper was 40.5 g. First layer of copper deposit are dense and the upper layer was dendrites and some copper powder also formed due to the copper concentration reduces [2]. Such deposit can be dissolved on anode in obtained acid solution and copper plating solution formed. The other way of copper plating solution recovery is dissolution in acid solution containing oxidizers (hydrogen peroxide or air bubbling) [3].

So working solutions can be recovered without reagent using only by electrochemical membrane electrolysis. The calculated energy consumption were 400 kWh/m^3 (20 Euro/m^3) for etching solution and 600 kWh/m^3 (30 Euro/m^3) for copper plating solution respectively.

On base of obtained results the investigated process was also used for waste water treatment. It was found that copper concentration can be reduced up to 0.05 g/l and lower.

4. Conclusions

The process of etching and copper plating solution recovery was proposed. It was found that membrane electrolysis method allow to recovery working solution for electroless copper plating. The calculated energy consumption for proposed method was 400 kWh/m^3 (20 Euro/m^3) for etching solution and 600 kWh/m^3 (30 Euro/m^3) for copper plating solution respectively.

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