Electrochemical Treatment of Jewelry Alloys of Gold in an Acidified Solution of Thiourea

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Etching and polishing of gold alloys is mandatory in the jewelry industry. Both chemical and electrochemical methods are based on dissolving the surface layer of the alloy with the appropriate complexing agent to form a brilliant surface. Commonly, a cyanide process has been used for chemical etching and polishing. However, it is untenable from a health and safety perspective. The purpose of this work is to study the operation of an anodic electrochemical treatment of jewelry alloys of gold in an acidified solution of thiourea. Using voltammetry, the ideal concentration ranges of thiourea and sulfuric acid were determined for etching, polishing and oxidizing. A functioning prototype is described which is used in the production of gold watches with great success.

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Etching of gold alloys is a mandatory operation after casting. It is realized for dissolving the surface layer of the alloy, in which during the casting irreversible changes of the quantitative composition have occurred, connected with oxidation of copper and other active components of the alloy. Etching is also necessary for removing traces of the material of the casting form from the surface of the alloy. Chemical and electrochemical methods of etching of gold alloys are known.

Polishing of jewelry alloys of gold is usually realized by mechanical, chemical or electrochemical methods. In the cases mechanical polishing cannot give proper results when products have recesses or uneven relief. Chemical or electrochemical methods are used in such cases.

Both chemical and electrochemical methods of etching and polishing are based on dissolving the surface layer of the alloy in the appropriate complexing agent that brings to the formation of a more or less brilliant surface under certain conditions.

The mixture of warm water solutions of potassium cyanide and hydrogen peroxide is used as an agent for chemical etching and polishing. The mixture is prepared right before carrying out the process and can be used one time only. When mixing the above mentioned solutions a rapid reaction with gassing of extremely toxic dicyan takes place. The solution contains cyanides and alkali. The process is too dangerous from ecological perspective. Its realization by unskilled personnel is unacceptable. Despite this fact this method of etching is widely spread because of simplicity of its application.

Chemical methods of etching and polishing are widely spread all over the world, e.g. USA, Arabic countries, Indo-China. In many countries, for example USA, these methods are forbidden because of intensification of environmental control. Gold and silverware producers who based on the technology have to conduct processing of the surface incurs huge penalties imposed by controlling organizations. Many of them transfer their businesses to Asian countries where requirements are not so strict.

Essence of the electrochemical method is anodic oxidation of the alloy components in the presence of a complexing agent. At the same time in micro ledges, where the current density and diffusion rate are higher dissolving happens faster than in cavities, and as a result the surface smoothes out. It is possible to use solutions of potassium cyanide, thiourea, etc. as complexing agents. At present mainly the solution of thiourea, acidified by sulfuric acid is used, considering extraordinary toxicity of cyanides.

Realization of electropolishing requires high professionalism. The solution often requires adjustment both by thiourea, and by sulphuric acid; the necessary temperature and voltage need to be selected. If an incorrect mode is selected non-repeatability of results is observed, outgassing of hydrogen sulphide takes place on the cathode, and these circumstances prevent this undoubtedly progressive method from being widely spread.

To solve this problem we have set the task to develop an automatic computer-aided system that will be able to control the process independently. For that purpose we have started to investigate anodic dissolving of alloys of gold in acidic solutions of thiourea.

Experimental

The first patent for the solution for electrochemical polishing of alloys of gold containing 50g/L of thiourea and sulphuric acid belongs to the company Degussa. All the further proposed non-cyanide electrolytes also contain thiourea, only its concentration differs. For example, according to the USSR Standard a solution containing 90g/L of thiourea and 40g/L of sulphuric acid was suggested for electropolishing. By the same Standard a solution containing 120g/L of thiourea and 60g/L of sulphuric acid was suggested for electroetching.

Because the data on the composition of electrolytes differs greatly we have conducted experiments with different solutions for electroetching and electropolishing in the Yerevan Factory of Art Watches.

We have studied the solutions with the following composition:

I. Thiourea 76g/L , Sulfuric acid 49g/L
II. Thiourea 90g/L , Sulfuric acid 49g/L
III. Thiourea 90g/L , Sulfuric acid 60g/L
IV. Thiourea 100g/L , Sulfuric acid 60g/L

All experiments have been conducted in stationary conditions with fixed electrodes and without stirring. Plates, frames of watches, bracelets as well as other jewelry made of an alloy of gold containing 58,5% Au, 33,5% Cu and 8,0% Ag have been used as an anode.

Results and Discussion

It is known that the first rectilinear portion of the anodic polarization curve corresponds with even dissolving of the metal. In the "wave" section electropolishing takes place and at higher voltage values oxidizing of the surface of the metal occurs [1].

The anodic polarization of the gold alloy in acidic solution of thiourea depends on the concentration of thiourea and sulphuric acid, as well as on the temperature of the solution (Fig. 1, 3, 6, 8).

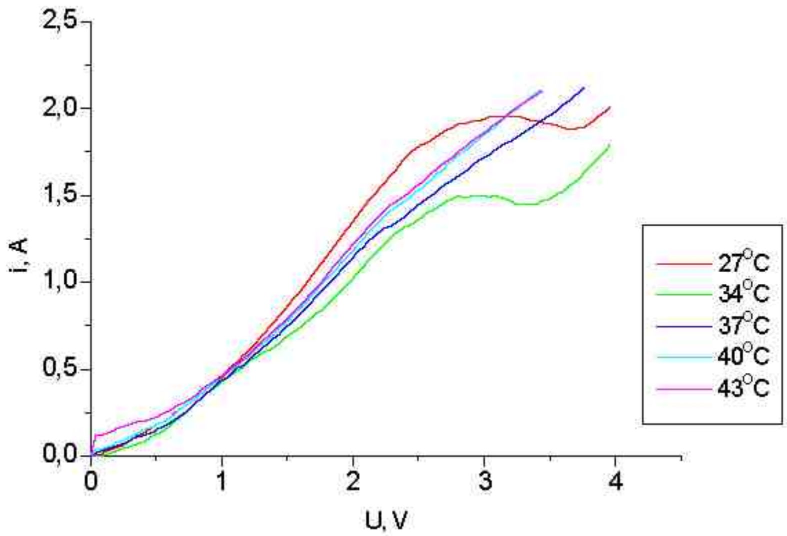

Fig.1. Dependence of anodic polarization on the temperature (solution I) .

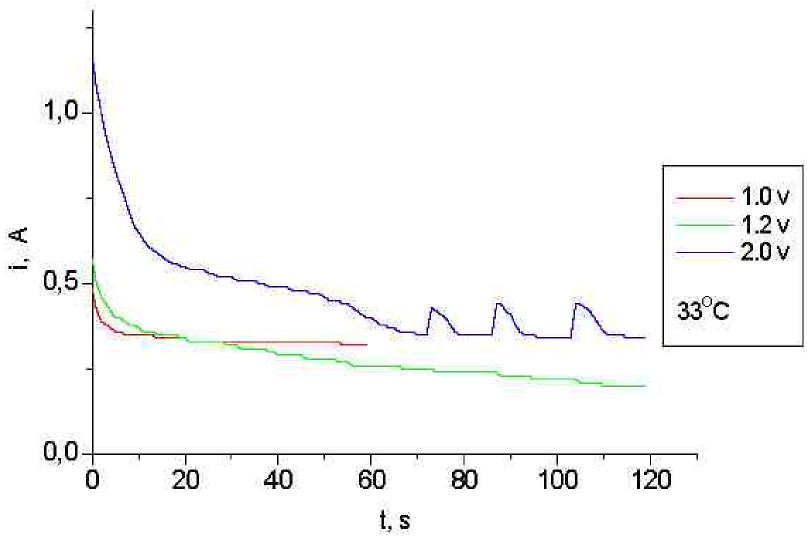

Fig.2. Current-Time dependence during the process of electrotreatment (solution I, 33°C).

Dissolving of the anode can be simplifiedly divided into the following stages:

In the first stage oxidation of the metal atoms takes place.

$$Au - e \longrightarrow Au^+$$
$$Cu - e \longrightarrow Cu^+$$
$$Ag - e \longrightarrow Ag^+$$

In the second stage complex forming with two molecules of thiourea occurs

$$Me^+ + 2\,SC(NH_2)_2 \longrightarrow Me[(SC(NH_2)_2]_2^+$$

In the third stage complexes are hydrating and diffusing into the solution

$$Me[(SC(NH_2)_2]_2^+ + n\,OH_2 \longrightarrow Me[(SC(NH_2)_2]_{2(aqua)}^+$$

A limiting stage is the diffusion of complexes from the surface into the solution and reverse diffusion of free ligands molecules. The diffusion rate greatly depends on the temperature, naturally the temperature must strongly influence the course of the process. It can be seen on Fig. 1. For example increasing the temperature above 37^{o}C results in disappearing of the "wave" at voltage of about 3V.

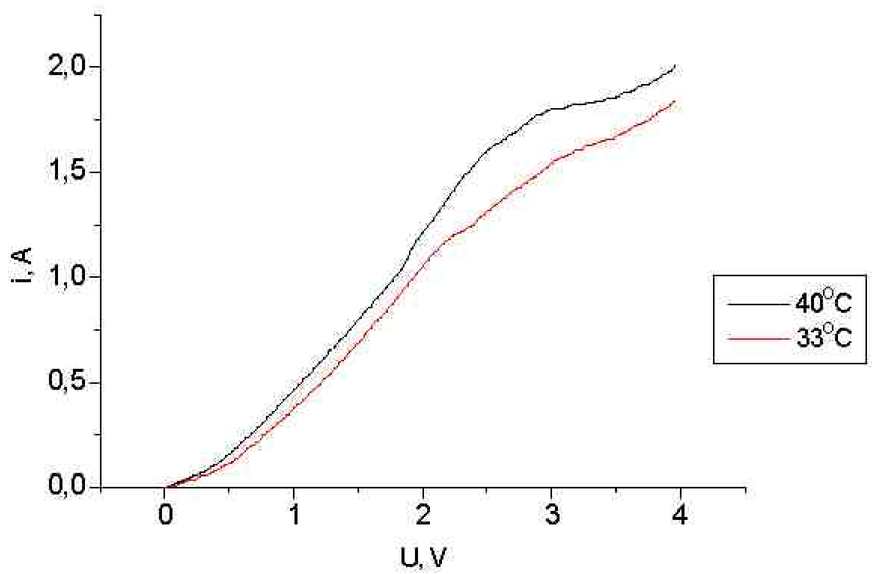

Fig.3. Anodic polarization curves at 33^{O}C and 40^{O}C,(solution II).

Increasing the concentration of thiourea from 76g/L to 90g/L doesn't essentially affect the shape of the curve (Fig. 3), but at 33^{o}C a clearly expressed periodic process is observed at the range of 1.6-1.8V (Fig. 4).

This can be explained by periodic formation and dissolution of the oxide film on the anode [2,3] when the rate of formation of oxides is approximately equal or a bit more than the rate of diffusion of ligands to anode.

When increasing the temperature the rate of diffusion increases so much that even increasing the voltage up to 3.6V results in a stationary process after only 15-20 sec (Fig. 5).

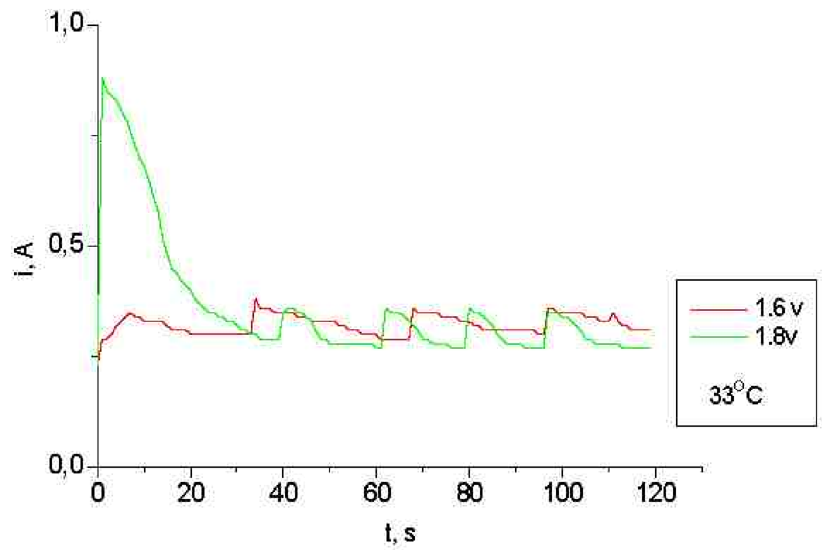

Fig.4. Current-Time dependence during the process of electrotreatment (solution II, 33°C).

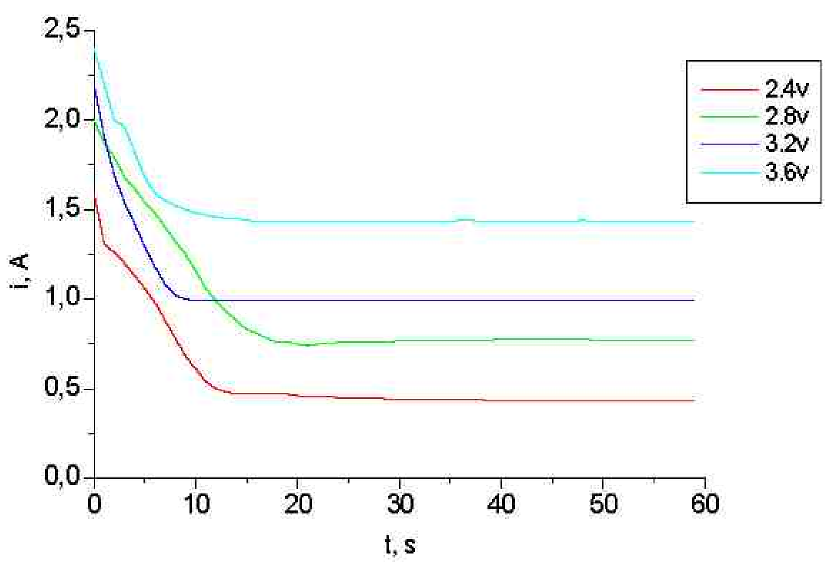

Fig.5. Current-Ttime dependence during the process of electrotreatment (solution II, 40°C).

The data for solution III is shown in Fig 6 and 7.

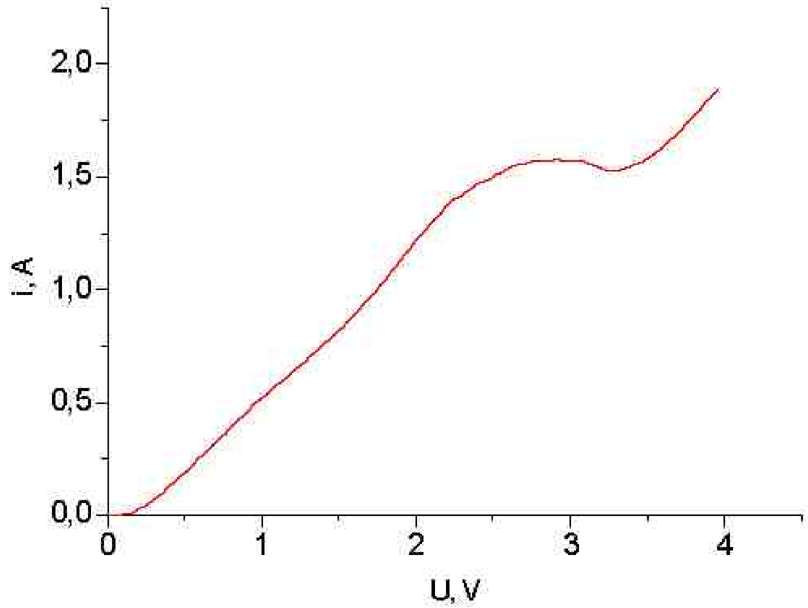

Fig.6. Anodic polarization curve at 40^{O}C (solution III).

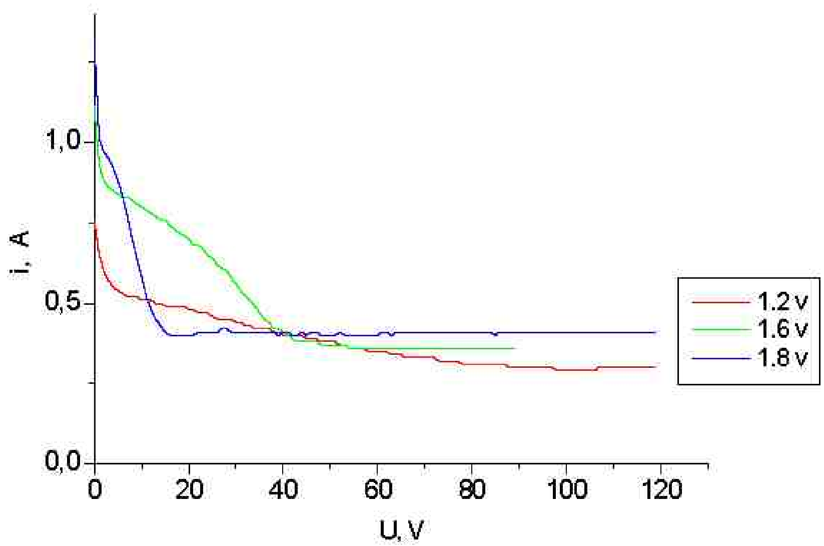

Fig.7. Current-Time dependence during the process of electrotreatment (solution III, 40^{O}C).

On Fig 8 and 9 a specific example of electropolishing of a bracelet in solution IV is illustrated.

At the temperature 25°C a wave is observed at voltage 3V.

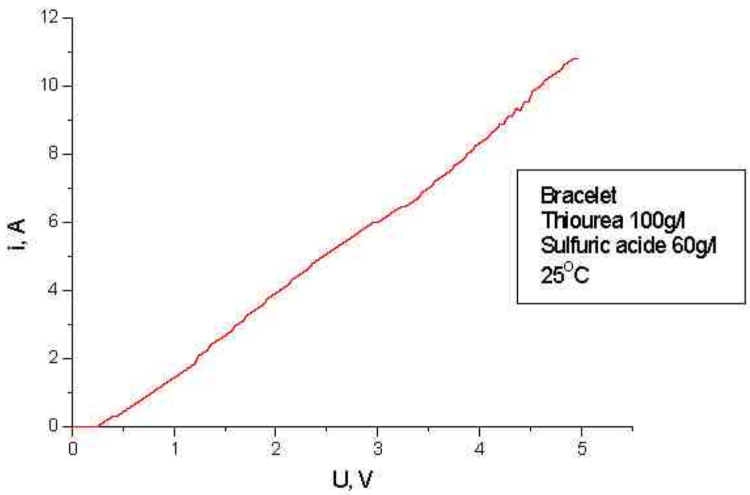

Fig.8. Anodic polarization curves at 25°C (solution IV).

2 minutes after starting electropolishing the periodic process starts. In three minutes only the product is polished so well that there is no need for mechanical polishing.

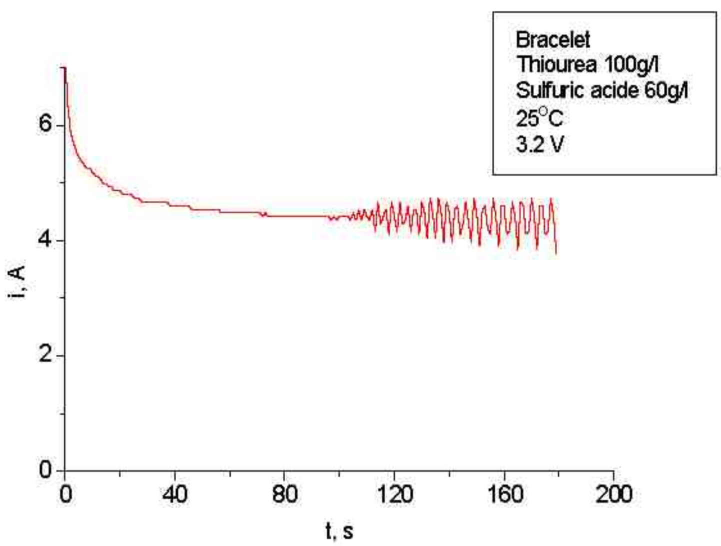

Fig.9. Current-Time dependence during electropolishing of bracelet (solution IV).

Summary and conclusions

Studies of the electrochemical dissolution of jewelry alloys of gold in thiourea-sulfuric acid solution show that the best results are obtained in case of the following composition of the solution: thiourea - 100 g/L and sulfuric acid – 60 g/L. This is a universal solution that can be used for all the processes - electroetching, electropolishing and oxidizing only by changing the conditions of electrochemical treatment (temperature, voltage, etc.).

Investigation of electrochemical dissolving patterns of gold alloys in the solutions of thiourea and sulphuric acid has shown that it is possible to create a device for electroetching, eletropolishing and oxidizing which will be able to independently, without intervention determine the optimal mode for conducting the process and automatically realize the process under the most appropriate conditions. So the advantages of chemical and electrochemical methods are combined in one device – simplicity, quality and repeatability.

Such a device will give the opportunity to obtain the maximum possible results with 100% repeatability.

- No expensive professional executers will be necessary.
- Isolation of gold from the electrolyte will take place on the cathode simultaneously as the process proceeds. And a separate operation for regeneration of gold from the solution won't be required.
- It will be possible to eliminate the emission of poisonous and harmful gases into the atmosphere.
- Neutralization of the electrolyte won't be needed because the electrolyte will work for an unrestrictedly long time. It will be a great achievement from the environmental protection perspective.
- The device will be of great demand at jewelry firms, because it will improve the quality of produced products; direct costs of etching and electro polishing operations will decrease; irretrievable losses of gold will reduce. A great progress in protecting the environment will be achieved.

Presently we have created a functioning prototype which is used in the production of gold watches with great success. This automatic device for electrochemical etching and polishing will allow all jewelry producers to realize the necessary operations without problems and large expenses.

Our approach will give the opportunity to design and develop similar automatic devices for electrochemical etching, polishing and oxidizing of practically all metals and alloys.

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