Microelectroforming for Medical Applications

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Abstract

The aim of the project was the development of an electroforming process for the production of medical implants out of gold. To prove the applicability of this technology, tympanostomy tubes were chosen as demonstrators.

These barbell-shaped tubes are usually produced mechanically; of silicone or, for higher therapeutic demands, of metal – gilded silver or gilded stainless steel. Gold electroforming of the tubes as an alternative manufacturing process would reduce the expenditures for the mechanical preparation and lower the corrosion susceptibility significantly.

To obtain electroformed gold tubes of the desired shape, the following steps are necessary: fabrication of a negative template by drilling holes with countersinks in an insulated aluminium sheet, electroforming process, removal of the aluminium by using a sodiumhydroxide solution.

For the optimisation of the shape and surface quality of the tubes respectively the simplification of the manufacturing process, various parameters were tested, e.g. aluminium quality and sheet thickness, type of insulation layer, substrate processing, hydrodynamic conditions, type of electroforming electrolyte, electrodes position, etc.

The manufactured tubes were characterised in view of thickness distribution, hardness, surface roughness and purity in comparison to mechanically produced reference tubes.

From the results obtained during the project it can be concluded that electroforming processes can be easily adopted for the manufacture of medical implants. The time-consuming electroforming process is by far compensated by the simultaneous production of an arbitrary number of implants.

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Introduction

The material gold which has been used for medical applications since many of thousands of years is now becoming more and more important in numerous modern medical treatments (1). As gold is known for its excellent corrosion resistance, tissue biocompatibility and high resistance to bacterial colonisation, it represents an attractive material for the manufacture of medical implants.

The manufacture of medical implants could enlarge the fields of application for electroforming processes considerably.

The starting point was the description of depositing gold-nanowires in the pores of an anodised aluminium surface (2). After the electrodeposition of a reinforcing gold layer, the aluminium is dissolved with lye. Applied to the project, it was tried to use a cheap and easy to machine base metal as template (like aluminium) for the electroforming process and remove it afterwards chemically. Before electrodeposition, the first step should be the simulation of the primary current density distribution along the template and if necessary optimise its shape. For initial experiments, the Tuebingen Myringotomy tube was chosen as demonstrator. It has an inner diameter of 1.5 mm, an outer diameter of 2.8 mm and a thickness of ca. 200 µm.

Experimental procedure

At the beginning of the project, it was decided that the type of implant to be electroformed should be the barbell-shaped so-called Tuebingen Myringotomy tube (see **figure 1**).

FIGURE 1: Tuebingen myringotomy tubes (from Kurz company, D-Dusslingen)

To obtain tubes of the desired shape, the following steps are necessary (see figure 2 and figure 3):

The negative template is produced by insulating an aluminium sheet (its diameter corresponding to the future length of the tube) on both sides; then a hole is drilled into the sheet (its diameter corresponding to the future outer diameter of the tube) and finally on both sides the insulation is removed at a diameter slightly higher than that of the hole (future top and bottom of the barbell). Then, the uncovered surface of the negative is nucleated with a gold solution and afterwards a starting layer from an electroless gold electrolyte is applied. Finally, the actual gold layer is electrodeposited from an electroforming electrolyte. After electroplating, the aluminium substrate can be easily removed by dissolving it in a sodiumhydroxide solution.

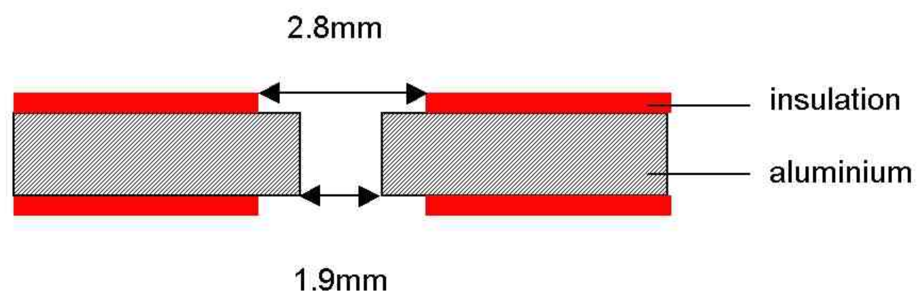


FIGURE 2: Schematic cross-section of the aluminium template

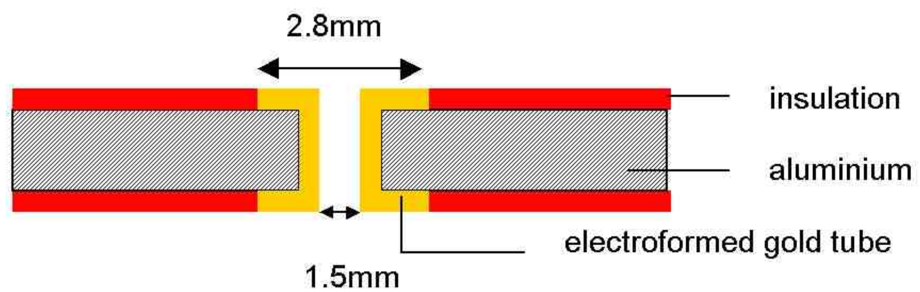


FIGURE 3: Schematic cross-section of the electroformed gold tube

Initial tests were executed based on [1] applying the following conditions:
At first, an anodised and an untreated aluminium sheet was nucleated with gold using a tetrachloroaurate solution and alternating voltage. After this, the starting gold layer was applied using an electroless gold electrolyte. Finally, the top gold layer was electrodeposited from an electroforming electrolyte. Subsequently, the alumina substrate was removed with sodiumhydroxide.
In the case of the untreated aluminium sheet a homogeneous, removable gold layer could be obtained.
Due to these promising results, it was decided to maintain the procedure in principle and to vary the following conditions in order to optimise the electroforming process respectively the shape of the tubes:

- substrate quality
- type of insulating layer
- substrate processing

– pretreatment procedure
– electroforming electrolyte
– hydrodynamic conditions

Experimental results

Simulation results

For the simulation of the electrodeposition process, the software Cell Design (Version 5, by L-Chem, Inc.) was used to determine the current density distribution at the cathode. The following figure 4 shows the current density in a cross-sectional view of the cathode (i.e. the aluminium substrate partly insulated having a drilled hole of 1.9 mm and a blank of 2.8 mm at top and bottom of the sheet).

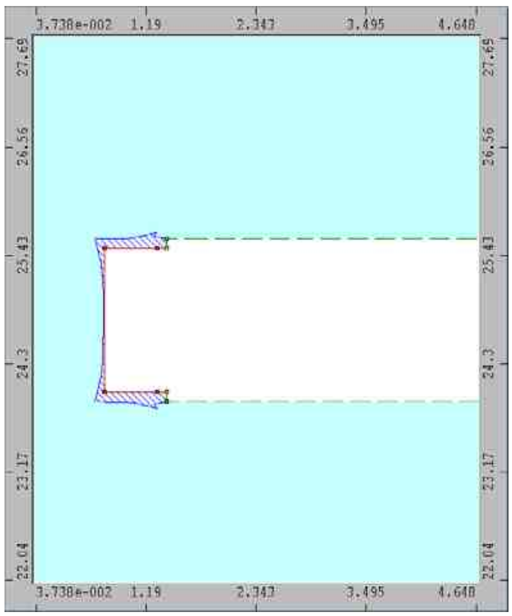


FIGURE 4: Current density map. The cross-hatched regions are proportional to the current density. The green regions represent insulated parts.

From these calculations, a tapering of the deposit thickness within the drilled hole becomes obvious. This can also be confirmed by the corresponding determination of the deposit thickness along the cathode (see figure 5).

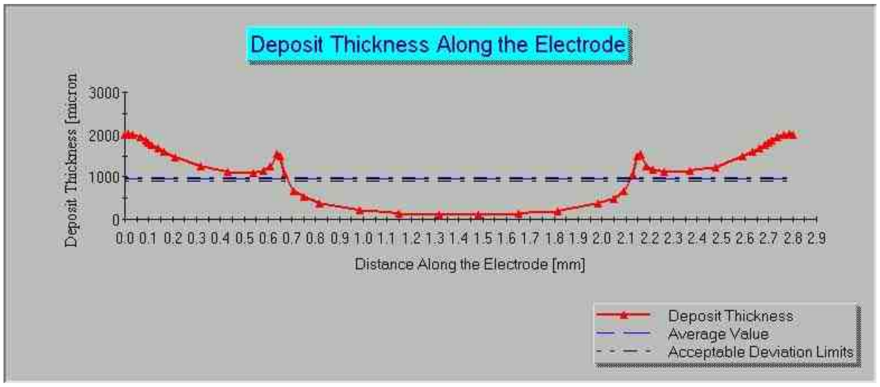


FIGURE 5: Deposit thickness along the cathode

Template material and type of insulating layer

Several aluminium qualities / alloys (thickness 2 mm) respectively several types of insulating layers on the template were tested.

In the case of powder lacquer, good results were obtained except the fact, that the thickness of the lacquer was only in the range of 110-120 µm. This means, that for a total thickness of 200 µm, the insulation has to be partly overgrown which might result in a loss of contour accuracy.

The use of an anodisation layer proved to be inadequate due to a lack of chemical resistance in the electrolyte with time. This fact is illustrated in the following SEM-pictures (figure 6 to figure 9).

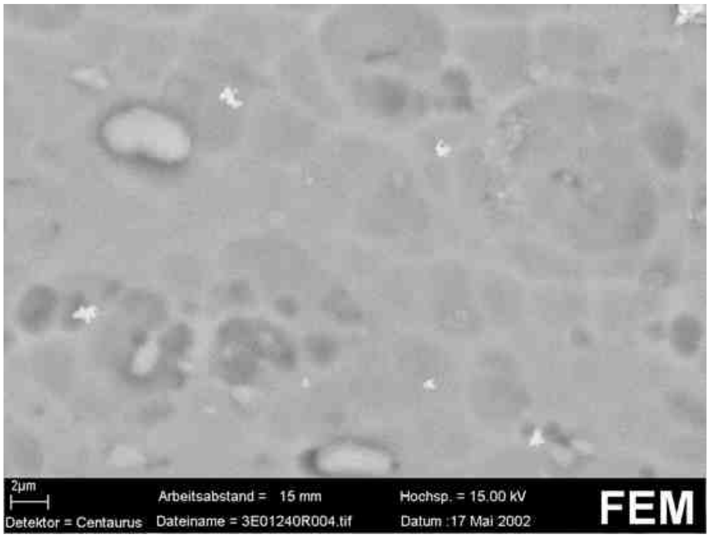


FIGURE 6: SEM-picture of an anodised aluminium surface (before immersion in the electrolyte)

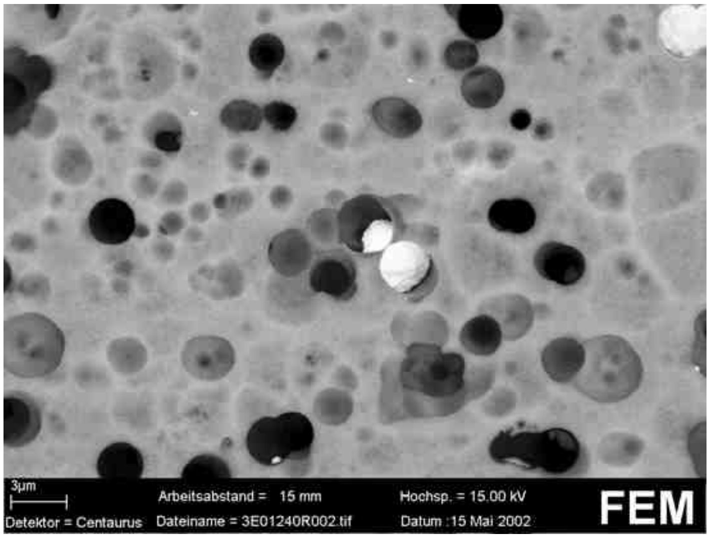


FIGURE 7: SEM-picture of an anodised aluminium surface (after several hours immersion in the electrolyte; no current)

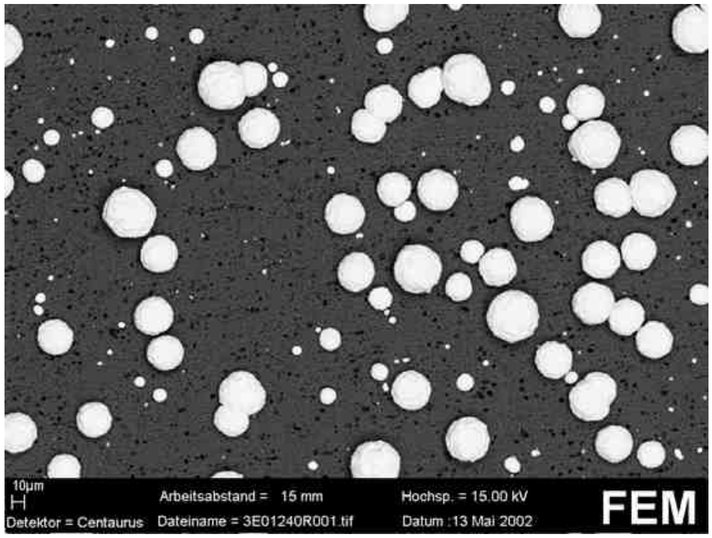


FIGURE 8: SEM-picture of an anodised aluminium surface (after several hours electrodeposition)

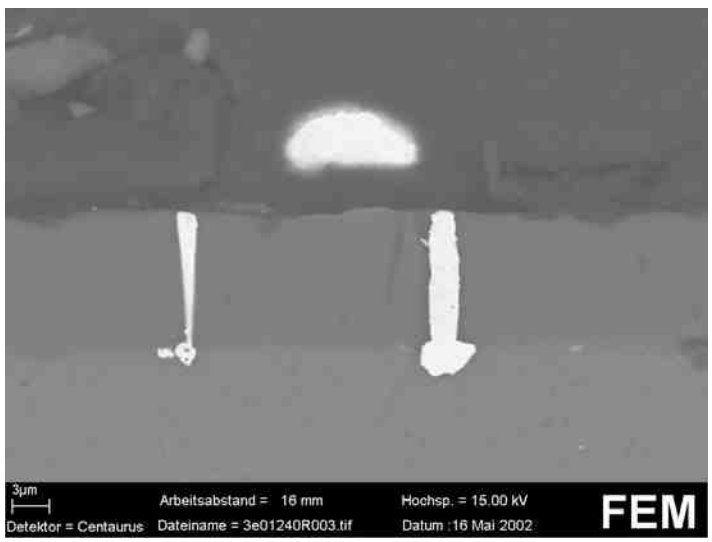
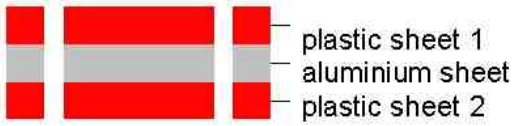


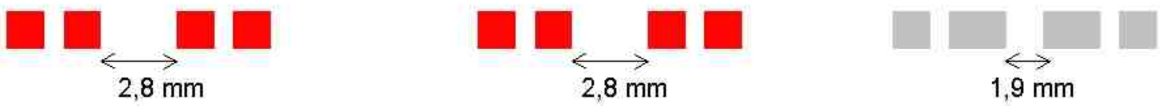
FIGURE 9: SEM-picture of a cross-section of an anodised aluminium surface (after several hours electrodeposition)

The installation of plastic sheets on both sides of the aluminium was verified as follows:

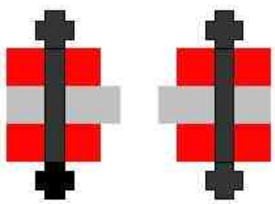
1) Fixing of the relative positions between plastic and aluminium sheets by drilling through



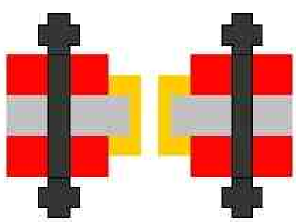
2) Separating of the sheets, drilling 2,8 mm holes in plastic and 1,9 mm holes in aluminium sheets



3) Assembly of the sheets by screw connections



4) Electroforming



5) Disassembly, dissolution of aluminium in sodiumhydroxide, plastic sheets are reusable

Template processing

During the project, the preparation of the aluminium templates turned out to be a decisive step in the manufacture of the tubes. At first, the templates were prepared by mechanical drilling which resulted in the occurrence of burrs (see figure 10).

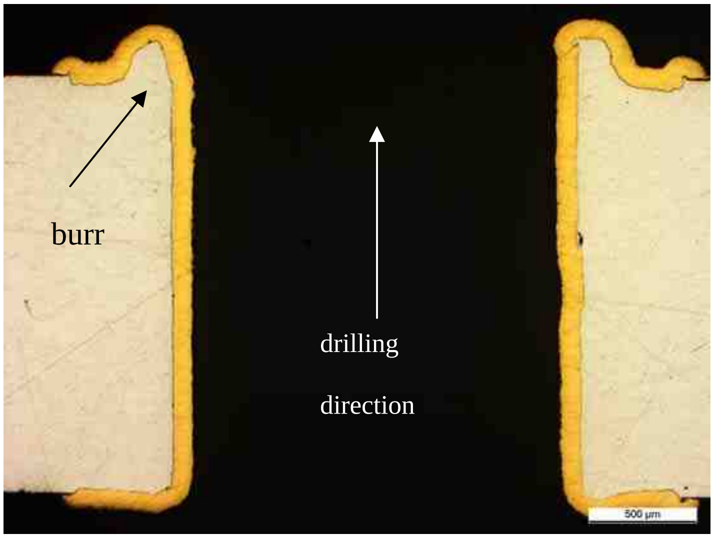


FIGURE 10: Cross-section of sample (template processing: mechanical drilling)

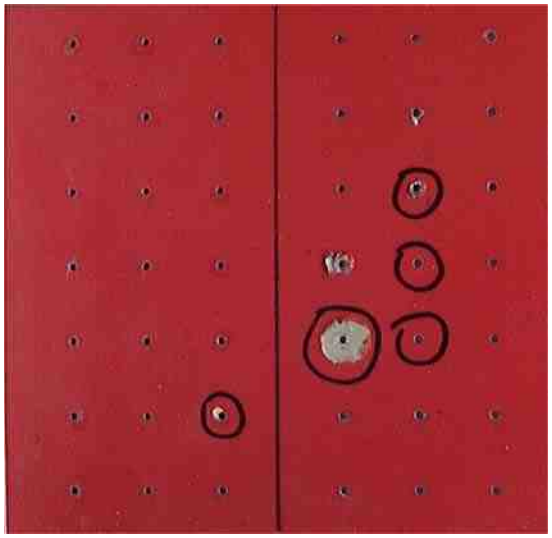


FIGURE 11: Lacquered AlMg1-sheet after laser drilling

Finally, the application of mechanical precision drilling gave best results in the substrate preparation, especially regarding the avoidance of burrs.

FIGURE 12: Left: Top view of lacquered aluminium sheet, after mechanical precision drilling; right: cross-section of template corner

Description of the electroforming electrolytes
The following table 1 lists the electroforming electrolytes and the corresponding process parameters.

TABLE 1: List of Electroforming Electrolytes

Electrolyte	Type of Au-complex	Temperature [°C]	pH value	Current density [A/dm^2]	Deposition speed [µm/min]
1	Au-cyanide	45	5,9	0,5	0,23
2	Au-cyanide	50	6,0	0,2	0,11
3	Au-sulphite	58	10	0,5	0,31

Electrodes position
The relative position of the electrodes was varied between parallel and inclined (see figure 13). In the case of an inclined position of the electrodes, the thickness distribution of the gold tubes became more homogeneous.

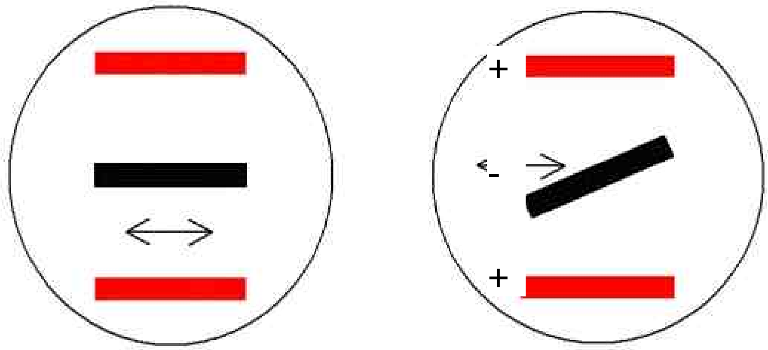


FIGURE 13: Top view of electrodes position in the electrolyte container (beaker); left: parallel, right: inclined (red: anodes, black: cathodes)

Hydrodynamic conditions

The influence of the hydrodynamic conditions on the quality of the tubes was examined. For this, samples were deposited in a beaker (with magnetic stirrer) respectively in a flow cell (see figure 14).

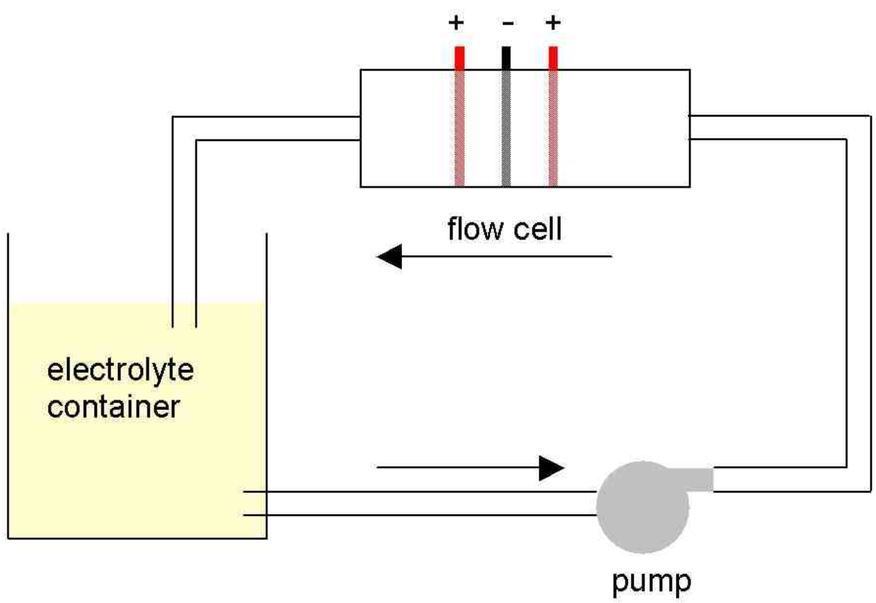


FIGURE 14: Flow cell (illustrated in a diagram)

According to initial experimental results, the anodes have to be triggered separately to obtain a homogeneous thickness distribution. The current density and the electrodeposition time at the inflow and the outflow anode were chosen in the ratio of 1 to 2.

Template removal
After electroforming of the gold tubes, the aluminium template has to be removed by dissolving it in a solution of sodiumhydroxide.

Post-treatment
Oxide residues on the surface of the tubes can be easily removed by dipping into diluted sulphuric acid.

Shape of the tubes
Depending on the electroforming electrolyte and the deposition conditions, different qualities of the outer appearance of the tubes were obtained. The following figures show pictures of the samples obtained from the different electrolytes.

Electrolyte 1
Beaker

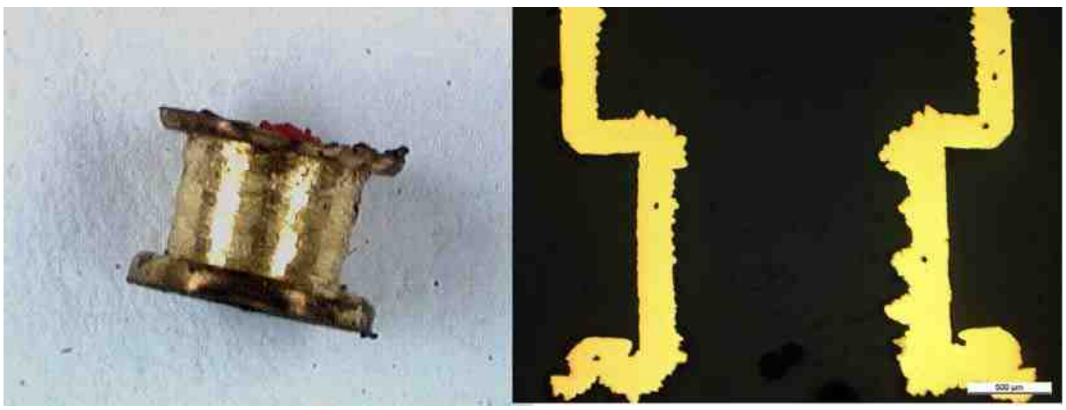


FIGURE 15: Myringotomy tube obtained from electrolyte 1; electrodeposition container: beaker

Flow cell

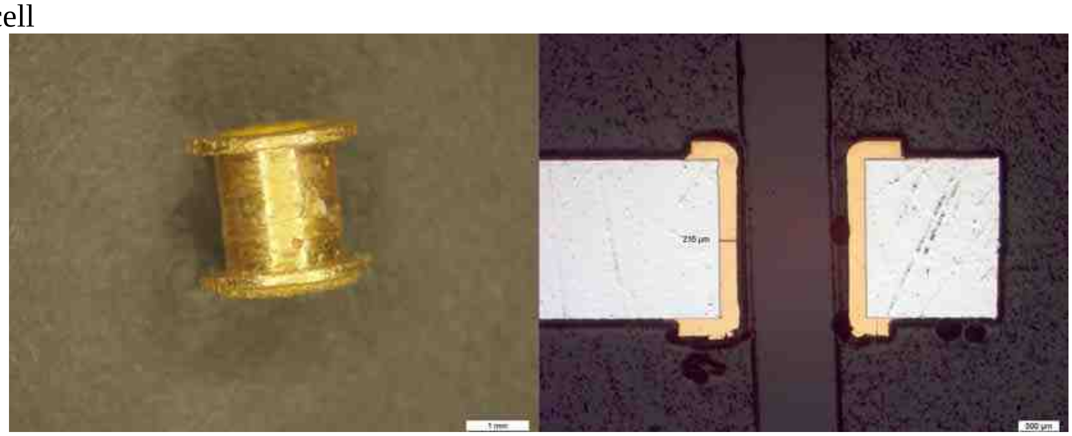


FIGURE 16: Myringotomy tube obtained from electrolyte 1; electrodeposition container: flow cell

Electrolyte 2

Beaker

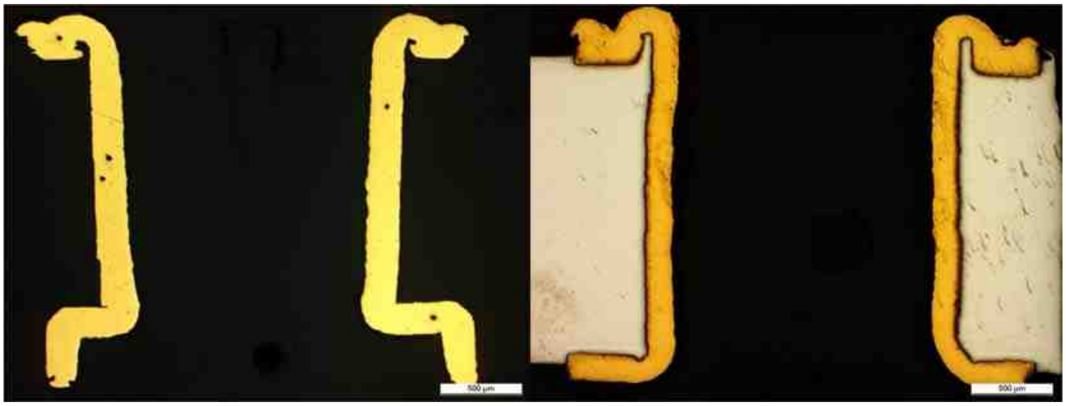


FIGURE 17: Myringotomy tube obtained from electrolyte 2; electrodeposition container: beaker

Flow cell

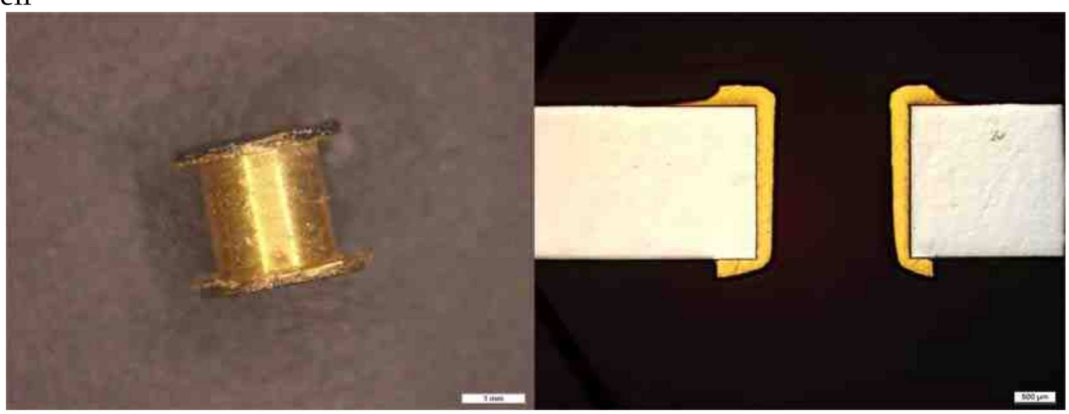


FIGURE 18: Myringotomy tube obtained from electrolyte 2; electrodeposition container: flow cell

Electrolyte 3

Beaker

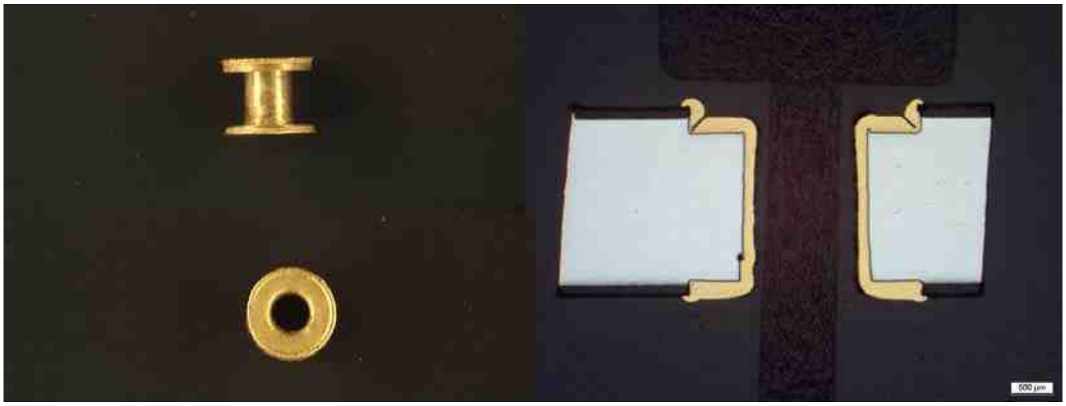


FIGURE 19: Myringotomy tube obtained from electrolyte 3; electrodeposition container: beaker

Flow cell

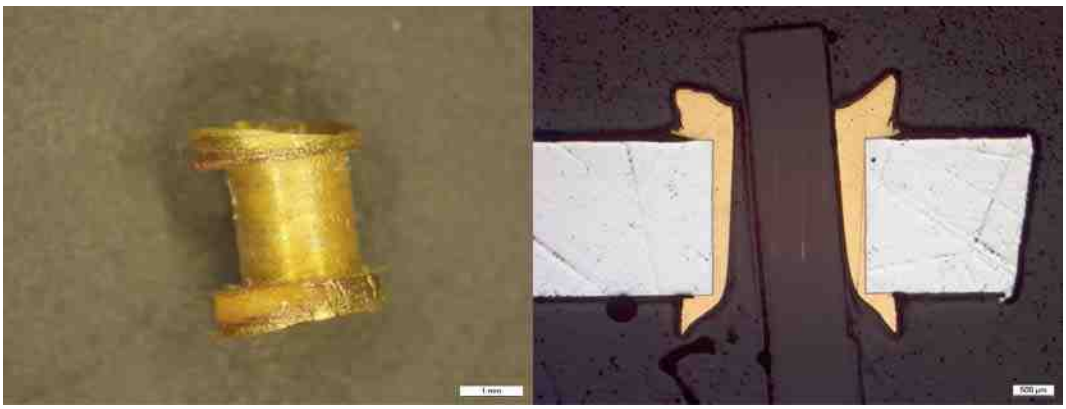


FIGURE 20: Myringotomy tube obtained from electrolyte 3; electrodeposition container: flow cell

Hardness

The hardness values (Vickers) for the samples deposited from the different electrolytes are listed below:

TABLE 2: Hardness of the Samples

Sample	Vickers hardness (HV0,05)
Electrolyte 1	75
Electrolyte 2	55
Electrolyte 3	82
Reference	129 (silver) resp. 131 (gold layer; HV 0,001)

In comparison with the reference samples (guilded silver), the hardness values of the electroformed tubes are quite low. This is not necessarily a disadvantage, as the only mechanical load the tubes have to withstand is the insertion in the ear drum.

Surface quality

The surface of the samples obtained from the flow cell experiments were characterised with EDS-analysis. The following spectra were recorded:

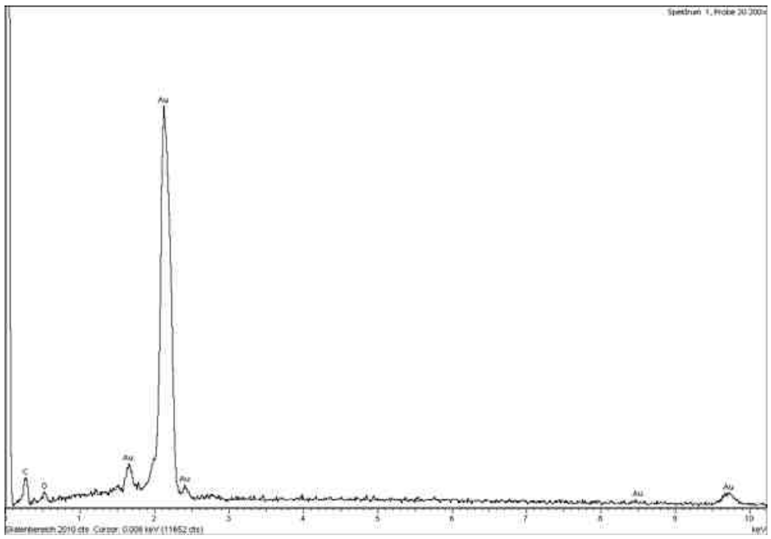


FIGURE 21: EDS-spectrum of sample obtained from electrolyte 1; electrodeposition container: flow cell

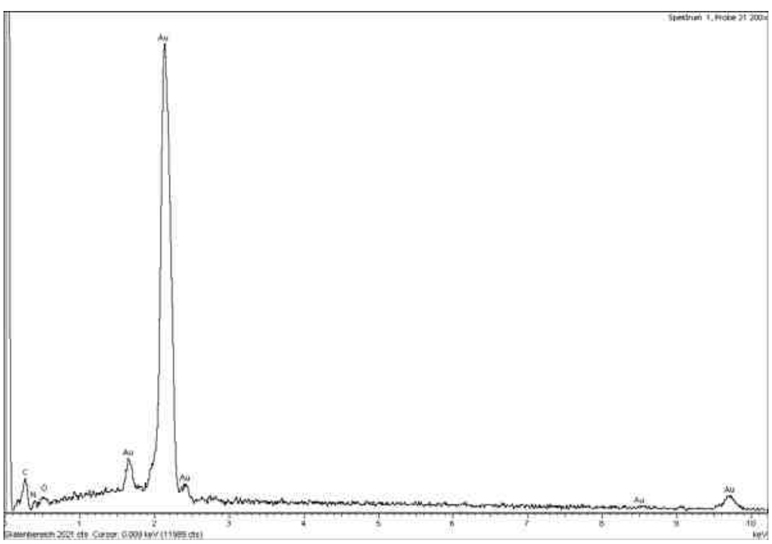


FIGURE 22: EDS-spectrum of sample obtained from electrolyte 2; electrodeposition container: flow cell

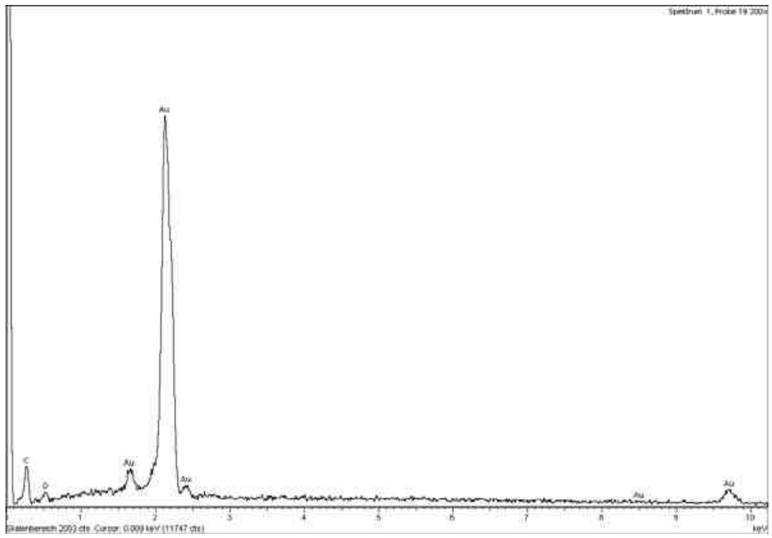


FIGURE 23: EDS-spectrum of sample obtained from electrolyte 3; electrodeposition container: flow cell

In order to be able to compare the results, also from an EDS-spectrum of the surface of a reference sample was recorded:

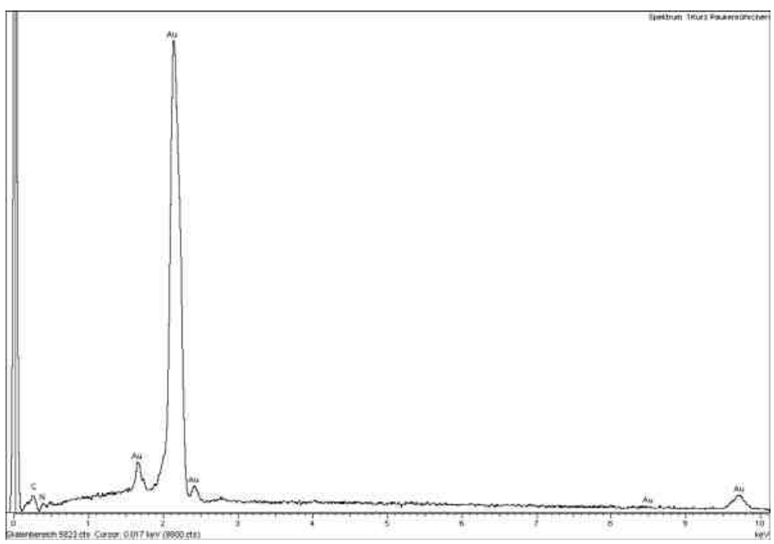


FIGURE 24: EDS-spectrum of reference sample (guilded silver)

In the case of the electrolytes 1 and 3, carbon and oxygen were detected; the spectrum of the electrolyte 2 shows carbon, oxygen and nitrogen peaks and on the surface of the reference sample carbon and nitrogen are identified.
The concentrations of the impurities are all in the same range.
Carbon and nitrogen may be due to the incorporation of cyanide; oxygen is probably due to the oxide formation during the template dissolution.

Discussion and conclusions

The results obtained during the project allow the following conclusions:

- electroforming as a manufacturing process for medical implants represents a good alternative to mechanical processes
- a large number of samples can be produced simultaneously, compensating the time-consuming electroforming duration
- a major factor for the quality of the tubes is the processing of the template; the so far applied mechanical drilling process provides a good quality, but could be further optimised for example by automated process steps
- the adaptability of the technique towards modifications in the product shape of the is very high
- electroforming could decrease the fabrication costs significantly by simultaneously lowering the infection susceptibility due to the use of fine gold

The demonstrator chosen for the project was the Tuebingen myringotomy tube. As the realisation of this type of implant by electroforming was very successful, the application of this technology could be expanded to other implant types.

Further, experiments are conceivable with gold alloy electrolytes; for instance gold-silver. Depending on the application, a tailoring of the properties may be required; for example an increased hardness increase may be realised by addition of grain refiners.

References

(1) Extracts from http://www.gold.org/discover/sci_indu/indust_app/biomedical.html

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