LETTER TO THE EDITOR

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Electrodeposition of ^{106}Ru and ^{241}Am and derived information on preparing sealed radiation sources

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The application of electrochemical plating method for the deposition of electropositive Ru and electronegative Am was examined. These investigations were aimed on the preparation of sealed radiation sources of ^{106}Ru used in treatment of intraocular tumours, and ^{241}Am used for ionization purposes. The composition of galvanic baths and process parameters influencing the quality and stability of ruthenium deposites and americium with gold co-deposites were determined. The effect of ageing of the electrolyte on the rate of ^{241}Am co-deposition was investigated. From the results obtained it follows that the ageing favours the formation of species affecting the transport of americium towards the cathode. The method of sealing of the sources by means of galvanic deposition of metallic protective layers is described. The galvanic plating technique enables manufacturing of sealed radiation sources of ^{106}Ru and ^{241}Am.

Introduction*

Superficial radiation sources are widely used in different types of isotopic apparatuses and also in nuclear medicine for radiotherapy of tumours. Ruthenium-106 besides ^{90}Sr, ^{60}Co and ^{125}I is applied in ophtalmic applicators for irradiation therapy of malignant choroidal melanoma.[1,2] The applicators are hemispherically shaped and contain the radioactive material fixed on the concave side of the shell made of silver 0.9 mm thick, which absorbs nearly 95% of the 3.5 MeV beta-radiation of ^{106}Ru. The thin film of radioactive material is coated with a metallic protecting layer or covered with brased window to exclude radioactive contamination.

Americium-241 sources are applied in smoke detectors and static eliminators. Electrolytic deposition of americium on the cathode as metal is impossible due to its highly negative standard oxidation potential. Galvanic plating enables, however, the incorporation of non-metallic solid phase into the cathodic deposits in a co-deposition process.[3] During the electrolytic co-deposition of americium with precious matrix metal, a cathodic layer hydrolysis can occur, with the formation of slightly soluble hydroxides or oxides having often the form of charged colloides or pseudocolloides which are included into the structure of growing metallic layer.[4,5] This method of fixing of ^{241}Am was investigated[6] from the point of view of manufacturing of radiation sources. Continued investigations of the co-deposition of americium-241 with gold concerned the effect of ageing of the electrolyte.

Experimental

From among many electrolytes examined in details for ruthenium plating, the aqueous solution of sulphamic acid containing ruthenium nitrosyl-trichloride was choosen. The concentrations were $Ru(NO)Cl_3$ – 5 g/l, $H_2N\text{-}SO_2\text{-}OH$ – 40 g/l. Ruthenium-106 with specific activity of about 75 GBq/g was added to this solution as chlorocomplex or nitrate. The total volume of the plating bath was 10 ml. Current density was 30÷50 mA/cm^2 and temperature 70 °C. Platinum anodes were used with the area of about 5 times greater than that of the cathode. Under these conditions, metallic, lustrous deposites without crakings were obtained.

To avoid the formation of volatile ruthenium tetroxide under strongly oxidising conditions at the anode, a special galvanic cell was designed in which the anolyte is separated from the catholyte. This cell enables also the deposition of ruthenium on the concave side of the shell with an 0.8–1 mm inactive edge.The fixing lugs remain inactive as well. Efforts with applying masking agents have clearly proved unsuitable.

Ruthenium deposites thus obtained were sealed either by brazing a front window of silver 0.1 mm thick on the concave side of the hemisphere or by galvanic plating. The galvanic method comprises nickel plating of the whole applicator and finishing with an outer layer of gold-cobalt alloy. The Au-Co platings[7] reveal relatively high microhardness ($\mu H_{10} = 150 \div 220$) and tightness. The porosity disappears already after reaching thickness of 0.5 μm. For both methods of sealing, the outer Au-Co plating is applied to warrant the contact of the tissue with homogeneous and inert material. The method of sealing used in manufacturing procedure should depend on the results of the safety tests performed in accordance with the ISO classification.

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Thermoluminescent dosimetry was applied for the dose rate measurements. Sintered detectors LiF:Mg,Ti with graphite, 0.7 mm thick and 4.5 mm in diameter were used. The detectors were annealed for 1 hour at 400 °C and for 2 hours at100 °C before each exposition. After the exposition and annealing for 10 minutes at 100 °C, the luminescence was measured in argon with a Harshaw 2000 AB, previously calibrated with reference light source.

In the continued investigations of Am with gold co-deposition, the effect of ageing of the electrolyte on the rate of co-deposition was examined. Alkaline cyanide baths (pH 11) containing constant concentrations of $K[Au(CN)_2]$ and ^{241}Am were used in each electrolysis. It can be assumed that in such medium americium forms colloidal or pseudocolloidal hydroxides such as $Am(OH)_3$, $Am(OH)_4$ or $Na_2AmO_2(OH)_3 \cdot nH_2O$.[8] Volume of the galvanic bath was 300 ml and the area of silver cathode 37 cm^2. Current density of 200 mA/dm^2 was applied. Each electrolysis lasted as long as to obtain the activity of 111 kBq/cm^2 (3 μCi/cm^2). The distribution of the suspension particle size relative to the time of ageing of the electrolytes was measured with the Pamas PMT-3500 particle sizer.

Results and discussion

The results presented relates to the applicators with an outer diameter of 15.5 mm. Ruthenium was deposited on the concave side of the shell on an area of 1.36 cm^2. The nominal activity shoul amount to 0.35 mCi±30%. In the first experiments performed, 10 ml of bathe solution contained 50 mg Ru and 10 mCi of ^{106}Ru tracer (specific activity about 2 Ci/g). After 30 minutes of plating, 2÷3 mg Ru was deposited, which corresponds to a coating thickness of about 1÷2 μm. The calculated and measured activities and dose rates are presented in Table 1. P1 and P5 applicators were sealed by brazing and subsequent gold plating, whereas the remaining ones by galvanic plating.

The dose rates measured at different spots of the active surface expressed in % relative to the centre of the applicator are shown in Fig. 1. It characterizes the uniformity of activity distribution over the surface area of the applicator.

The dose rate values of beta-radiation as a function of distance from the centre of the concave side of the applicator are presented in Fig. 2.

As the thickness of the detector used was 0.7 mm, the least distance from the surface of the applicator was 0.35 mm. The extrapolated value to the zero distance (Fig. 2), should be considered only as approximative.

To determine the influence of ageing of alkaline bath solutions on the rate of co-deposition of americium with gold, seven separate electrolytes were prepared. First electrolysis was performed immediately after preparing the bath solution, next after a period of ageing at ambient temperature (~23 °C).

Table 1. Characteristics of some prototype applicators

No.	Mass of Ru, mg	Thickness, μm	Calculated activity, mCi	Measured activity, mCi	Dose rate,* mGy·min^{-1}
P1	3.05	1.8	0.61	0.44	80
P2	3.15	1.9	0.63	–	210
P3	2.70	1.6	0.54	0.51	236
P4	2.55	1.5	0.51	0.57	221
P5	3.50	2.1	0.70	0.50	163
P6	2.70	1.6	0.54	0.56	236

* Tolerance: ±20% (2σ)

Table 2. Ageing period, co-deposition rate and time of electrolysis indispensable for obtaining constant activity

Ageing time, temperature, days		Co-deposition rate, μCi/min	Time of electrolysis, min	Activity, μCi/cm^2
40	amb.	6.4	18	3.1
30	amb.	5.3	20	2.9
10	amb.	3.9	29	3.0
10	0 °C	1.3	86	3.0

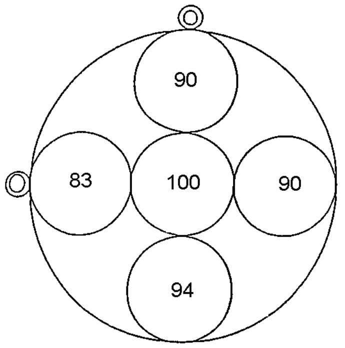

Fig. 1. Surface dose rate distribution in percentage of the value in the centre

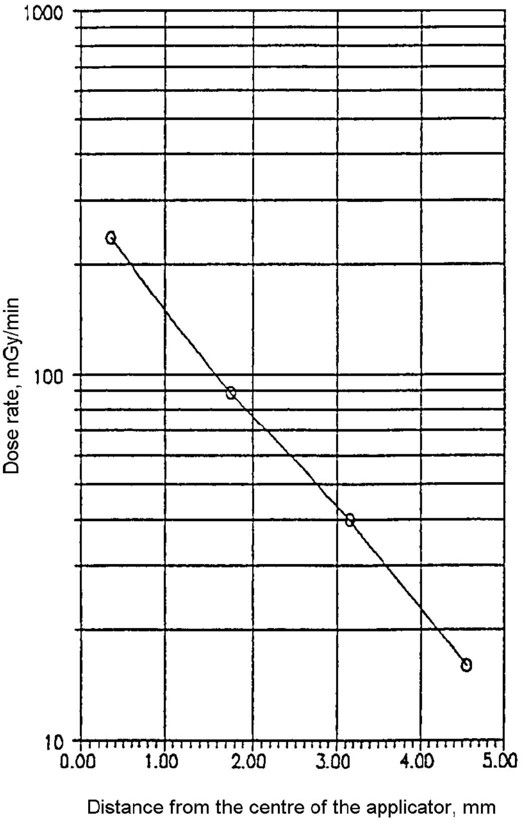

Fig. 2. Dose rate at different distance from the centre of the applicator

Duration of each electrolysis was so adjusted as to obtain constant activity of 3 μCi/cm^2 of the cathode. As it follows from Fig. 3, the rate of co-deposition increases with time of ageing up to about 40 days, and then slows down.

Fig. 3. Rate of Am/Au co-deposition vs. time of ageing of the bath solution at ambient temperature

As it can be seen from the data collected in Table 2, the plating time can be decreased with increasing period of ageing, to receive the assumed constant activity of 3 μCi/cm^2. Also the temperature of ageing affects the co-deposition. The increase of co-deposition rate is lower when the bath solution was aged at 0 °C as compared with that at ambient temperature.

These electrolytes were used for galvanic co-depositions in which the plating time necessary to obtain the activity of 3 μCi/cm^2 was registrated. As it follows from Fig. 4, the rate of co-deposition decreases in each successive plating although the concentration of the bath components was held constant. To reach the assumed activity, duration of electrolysis must be extended. Different situation occures when ageing proceeds at 0 °C. In such case the rate of co-deposition increases, and shorter times of plating can be applied. It can suggest that at 0 °C ageing does not occur or proceeds extremly slow and the formation of species responsible for the rate of co-deposition takes place during the exploitation of the electrolyte at ambient temperature. Then presumable the ageing process begins.

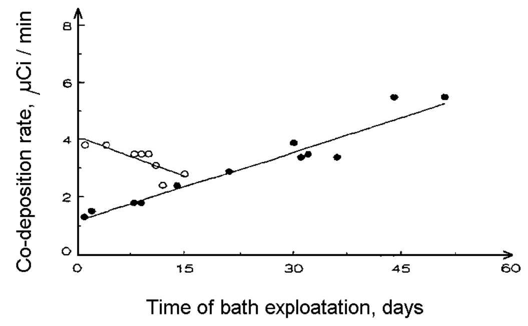

Fig. 4. Rate of co-deposition in successive platings; temperature: ○ ambient, ● 0 °C

The particle size measurements indicate that in freshly prepared electrolytes species 3 μm in diameter predominates, growing slightly with ageing time, due to agglomeration, up to 15 μm

Conclusions

From the investigations performed it follows that electrochemical plating can be applied for fixing radionuclides with both positive as well as highly negative standard oxidation potentials. Such method can be considered as useful in manufacturing sealed radiation sources. Galvanic plating enables also the sealing of sources by means of covering the radioactive deposite with protective layers of inactive metals. The effect of ageing of electrolytes from which co-deposition occures has been confirmed. On the basis of the results obtained from these experiments, sealed radiation sources of ^{106}Ru and ^{241}Am can be prepared. This method assures good uniformity of activity distribution over the surface area of the sources, which was confirmed by the dose rate measuremants of ^{106}Ru sources and ionization current of ^{241}Am sources.

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References

1. P. K. LOMMATZSCH, Survey Ophtalmol., 19 (1974) 85.
2. R. SEALEY, P. L. M. LE ROUX, F. RAPLEY, E. HERING, D. SHACKLETON, D. SEVEL, Br. J. Radiol., 49 (1976) 551.
3. J. P. CELLIS, J. R. ROOS, C. BUELENS, J. FRANSAUER, Trans. Inst. Metal Finish, 69 (1991) 133.
4. M. MIELCARSKI, M. PONINSKI, U. LORENS, Appl. Radiation Isotopes, 45 (1994) 429.
5. M. MIELCARSKI, J. Radioanal. Nucl. Chem., 205 (1996) 135.
6. M. MIELCARSKI, Electron Technol., 27 (1994) 155.
7. J. SOCHA, Galwanotechnika metali szlachetnych, Libra, Warszawa, 1991.
8. J. M. KULJAKO, T. I. TROFIMOV, D. A. MALIKOV, I. A. LEBEDEV, B. F. MIASOEDOV, Radiokhimia, 34 (1993) 68.