

# Thick silver electrodeposition on copper substrate for $^{109}\text{Cd}$ production

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Silver electrodeposition on copper substrate was investigated for production of  $^{109}\text{Cd}$ . The electrodeposition experiments were carried out by the alkaline plating baths. The optimum conditions of the electrodeposition of silver were: 4.1 g/l silver, pH 10–12, DC current density of ca.  $4.27 \text{ mA}\cdot\text{cm}^{-2}$  at 40–50 °C temperature with 100% current efficiency.

## Introduction

Cadmium-109 is a radionuclide that can be used as an X-ray fluorescence source. It has a half-life of 462.6 days and decays by electron capture to  $^{109m}\text{Ag}$  with  $\gamma$ -ray emission of 88.03 keV (3.79%) along with characteristic X-ray from the K level of Ag, with an energy of 22.54 keV (102%).<sup>1</sup> This radionuclide can be employed for calibration of detectors and as a radioactive tracer of Cd.<sup>2–9</sup> It can also be used in the energy dispersion X-ray fluorescence (EDXRF) technique.<sup>10,11</sup>

Cadmium-109 has found application in physiological research on animals and plants for more than forty years which has provided useful informations. This radionuclide can probably be used for inhibition of liver cancerous cells,<sup>12,13</sup> as well as for tissue imaging with SPECT (single photon emission computed tomography).<sup>14</sup> Additionally, it can be used to investigate the ecosystem.<sup>15</sup>

The production of  $^{109}\text{Cd}$  with a proton beam can be performed by reactions:  $\text{In}+\text{p}$ ,<sup>16</sup> that needs an energy of about 96 MeV,  $\text{Ag}+\text{d}$ <sup>17</sup> with energy 13.4 MeV and  $\text{Ag}+\text{p}$ ,<sup>18,19</sup> with an energy range between 14 and 9 MeV. Cyclotron is ideal for this work. Accelerator production of  $^{109}\text{Cd}$  is largely achieved via nuclear reactions  $^{109}\text{Ag}(\text{p},\text{n})^{109}\text{Cd}$  and  $^{109}\text{Ag}(\text{d},2\text{n})^{109}\text{Cd}$  which are well suited for medium to low-energy cyclotrons. Our centre in Karaj employs a Cyclone-30 (IBA, Belgium). Solid targetry systems on these accelerators are made of pure copper backing onto which target materials are electrodeposited.

It is noted that silver electrodeposits prepared from nitrate solutions, free of any organic or inorganic additive, are not smooth or compact, regardless of plating condition used. They consist of grains growing independently of each other and under given plating conditions may degenerate as dendrites.<sup>20</sup> Since most of the work directed at replacing cyanide in silver plating

has resulted in little more than technical interest,<sup>21</sup> for this work cyanide bath was chosen.

Silver cyanide baths usually consist of silver cyanide, potassium cyanide and sodium carbonate.<sup>22,23</sup> Carbonate and hydroxyl ions help to improve conductivity but they also help to prevent breakdown of cyanide by maintaining an alkaline pH. Free cyanide is necessary to improve the conductivity of the bath, it increases cathode polarization and thereby increases the throwing power.<sup>24</sup>

## Experimental

To take full benefit of excitation function and to avoid the formation of the radionuclidic impurities, the proton entrance energy should be 14 MeV.<sup>18,19</sup> The physical thickness of the silver layer is chosen in such way that for a given beam/target angle geometry the particle exit energy should be 5 MeV. According to SRIM code (The Stopping and Range of Ions in Matter),<sup>25</sup> the thickness has to be 352  $\mu\text{m}$  for 90° geometry. To minimize the thickness of the silver layer, a 6° geometry is preferred, in which case a 35  $\mu\text{m}$  layer is recommended.

Silver targets are prepared by DC-CCE (constant current electrolysis) of the metal from alkaline plating solutions.

An electrolysis solution is a volume of about 450 ml and a composition of  $5.1 \text{ g}\cdot\text{l}^{-1}$   $\text{AgCN}$ ,  $5.1 \text{ g}\cdot\text{l}^{-1}$   $\text{KCN}$ ,  $3 \text{ g}\cdot\text{l}^{-1}$   $\text{Na}_2\text{CO}_3$ , while the current between the electrodes is adjusted to 0.05 A. The silver electroplating was performed in constant current. In 2 hours, a silver target of  $36.75 \text{ mg}\cdot\text{cm}^{-2}$  thickness is prepared. Prior to the silver plating and to ensure a good adhesion, copper plate was cleaned using sandpaper of 1000 grade followed by rinsing copper plate with deionized water.

Non-reactive plating vessels are hollow Perspex cylinders (diameter 6 cm, height 20 cm) fitted with an axial Pt anode wire mounted at the bottom by means of a tube-end fitting with perforated septum.

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Four symmetrical windows (22.36 or 11.69 cm<sup>2</sup>) on the vertical side wall allow up to four copper targets backing positioning. Each slot is sealed by an O-ring fitted window. The geometrical shape of the slot determines the actual target electrodeposition area. The liquid-tight sealing of the windows is realized by stainless steel mechanical pestles mounted on a PVC ring surrounding plating vessel and by pressing the copper backing against O-ring seal. An external PVC ring is fitted with four supporting pins to hold a motor-stirrer combination in position. The stirrer is a hollow perforated POM cylinder mounted on the axis of a DC motor and surrounding the platinum anode. The stirrer rotation speed is set at 600 rpm; during the process, its rotating direction is reversed after 8 seconds improving deposit homogeneity. To keep the desired temperature at a preset level, a heater (a series of six isolated 1  $\Omega$ /W resistors, through which an appropriate DC-current is forced (1.1 A, 40 °C up to 1.8 A, 60 °C) is circularly mounted at the bottom of the vessel. An insulated sensor, introduced through the stirrer support-plate, monitors the plating bath bulk temperature. As electrolysis to depletion requires long-time (up to 24 hours) plating, evaporation of plating solution occurs. To maintain a constant liquid volume (450 ml), a conductivity glass/graphite sensor monitors the solution level and actuates a peristaltic pump at the required rate, supplying distilled water to compensate evaporation losses. The rack-mounted home-made electronics includes a motor/stirrer control, an adjustable DC voltage generator card and four V/I converters coupled to current boosters.

The freshly prepared solution of silver was poured into the plating vessel. This refined procedure is a result of several repeated experiments with different acidity and compositions of bath, different temperature and electroplating currents.

The morphology of all electrodeposited Ag target layers were examined in by a scanning electron microscope (SEM) (using a Joel Model JSM 6400 at an accelerating voltage of 20 kV).

The thermal shock tests involved the heating of the target up to 500 °C (the temperature that the Ag layer

can experience during a high current irradiation) for 1 hour followed by submersion of the hot target in cold (8 °C) water.

## Results and discussion

In order to optimize the Ag electrodeposition the experimental conditions were investigated as follows:

### *Influence of current density*

Since large amount of free cyanide in the bath forms a sedimentary layer on the Ag electrodeposition and consequently reduces the current efficiency, adjusting the quantity of free cyanide in the bath is important.<sup>26</sup> On the other hand, less amount of free cyanide reduces the bath conductivity. Hence, the bath compounds should be optimized. According to some publications on concentrations of silver in the bath,<sup>21–26</sup> a bath with 10.5 g·l<sup>-1</sup> AgCN, 7 g·l<sup>-1</sup> KCN and 3 g·l<sup>-1</sup> Na<sub>2</sub>CO<sub>3</sub> was prepared. The data provided in Table 1 denote a poor current efficiency at high current density but also formation of chalk-white sediment on the Ag deposit. Because low cathode efficiency results in low temperature, high current density and high free hydroxide,<sup>27</sup> while application of a very low current density results in a rather poor quality of the deposit, and a very high current density reduces the over voltage of hydrogen and decreases the quality and the current efficiency.<sup>28</sup> Hence, an optimal value was expected and investigated.

The current efficiency was determined at different current densities using DC current at room temperature (Table 1). An optimum DC current density of 4.27 mA·cm<sup>-2</sup> should be applied. Consequently, further experiments were carried out while using current density of 4.27 mA·cm<sup>-2</sup>, and changes were applied to the concentrations of bath compounds which consist of 8.5 g·l<sup>-1</sup> AgCN, 8.5 g·l<sup>-1</sup> KCN, 3 g·l<sup>-1</sup> Na<sub>2</sub>CO<sub>3</sub>. After changing the concentrations of the bath, the influence of acidity on current efficiency was concerned in further experiments. These alternations had stopped the undesired production of chalk-white sediment on the surface.

Table 1. Influence of current density, 10.5 g·l<sup>-1</sup> AgCN, 7 g·l<sup>-1</sup> KCN, 3 g·l<sup>-1</sup> Na<sub>2</sub>CO<sub>3</sub> solutions, 24 °C

pH	$J$ , mA·cm <sup>-2</sup>	Time, h	$t_0$ , μm	$t_C$ , μm	Current efficiency, %	Comment
10.00	17.094	0.83	33.40	33.30	61.1	Rough
10.00	12.82	1.50	49.40	49.24	67.0	Rough
10.27	8.54	1.30	26.29	24.33	57.0	Rough
10.00	4.27	2.00	31.52	31.02	100	Reflective, smooth
10.00	4.27	3.50	59.83	61.55	100	Reflective, smooth

$t_0$ : Mean thickness of the deposit in μm.

$t_C$ : Mean thickness of the deposit in μm after CIF cleaning.

### Influence of pH

Adjusting the bath acidity is important for the effect of bath efficiency and coating physical properties. A large reduction on acidity causes hydrogen reduction and simultaneously sediment of the basis salts on cathode. After preparing the silver bath (while the pH of bath was about 11) for studying the effects of solution acidity on electroplating quality, the acidity was changed from 8.5 to 13. It is clear that the higher current efficiency and the better electrodeposited layers are available in lower acidity than it is in comparison to electrodeposited layers by higher acidity bath (Table 2).

### Influence of temperature

Increasing the temperature of the solution increases the mobility of the ions and reduces the viscosity of the solvent. As a result it reduces concentration polarization and thus enhances the quality of the deposit (fewer tendencies to dendrite formation) and the current efficiency.<sup>28</sup> The mean current efficiency was 100% at a current density of  $4.27 \text{ mA}\cdot\text{cm}^{-2}$ , 40–50 °C temperature and time of 2 hours (Table 3).

### Pretreatment of the Cu-backing

Silver is a relatively noble metal; most metals being less noble than silver form immersion deposits on the surface. This tends to happen even when the base metal enters the silver solution hot or live, that is, with a voltage already applied. The inevitable result of this phenomenon is poor adhesion of subsequent deposits. To minimize this effect, it is essential to employ a silver strike coating prior to the main deposit.<sup>21,24</sup> In this work experiments were carried out on adhesion with and without strike coating. It was concluded that if the plating were carried out very rapidly, a good adhesion would be obtained in all electroplated targets without the need for strike coating.

Embrittlement of metals has been recognized for many years but, as two authors have pointed out, some other defects in electrodeposits, such as blistering, cracking, gas pits, peeling off and poor adhesion, may also be related to hydrogen in ways not yet identified.<sup>26</sup> Plating on a dietary or greasy surface inevitably leads to blistering or peeling of deposit. Cathodic cleaning in either acid or alkaline solutions provides large quantities of hydrogen for absorption.<sup>26</sup> In all experiments, the substrate surface was cleaned with sandpaper of 1000 grade and immersed in the nitric acid bath of 0.3M. Then the surface was washed by water and its oil contaminators were removed by a mixture of the alkali cleaning powders. Finally, the surface was washed with acetone.

Table 2. Influence of acidity,  $8.5 \text{ g}\cdot\text{l}^{-1}$  AgCN,  $8.5 \text{ g}\cdot\text{l}^{-1}$  KCN,  $3 \text{ g}\cdot\text{l}^{-1}$   $\text{Na}_2\text{CO}_3$  solutions, 24 °C, current density  $4.27 \text{ mA}\cdot\text{cm}^{-2}$ , 2 hours

pH	$t_0$ , $\mu\text{m}$	$t_C$ , $\mu\text{m}$	Current efficiency, %
8.5	26.94	26.37	81.0
9.0	29.32	29.00	85.0
10.0	31.33	31.29	97.1
10.4	25.07	24.74	88.8
10.5	30.41	30.17	92.0
11.0	31.80	31.12	97.0
11.5	32.91	32.84	100
12.0	33.84	32.72	100
12.3	33.27	32.78	99.8
12.6	33.01	32.55	100
13.0	33.64	31.21	86.7

Table 3. Influence of the temperature,  $8.5 \text{ g}\cdot\text{l}^{-1}$  AgCN,  $8.5 \text{ g}\cdot\text{l}^{-1}$  KCN,  $3 \text{ g}\cdot\text{l}^{-1}$   $\text{Na}_2\text{CO}_3$  solutions, pH 10–12, current density  $4.27 \text{ mA}\cdot\text{cm}^{-2}$

$T$ , °C	pH	Time, h	$t_0$ , $\mu\text{m}$	$t_C$ , $\mu\text{m}$	Current efficiency, %
24	10	3.5	49.20	48.77	85.0
40	10	3.5	53.72	53.15	92.7
24	10	2.0	30.21	29.32	89.4
35	10	2.0	32.55	32.34	98.6
40	10	2.0	33.21	33.13	98.0
45	10	2.0	31.69	31.36	95.6
24	12	3.5	57.33	57.29	100
40	12	3.5	57.19	56.21	98.0
24	12	2.0	33.04	32.38	98.7
35	12	1.9	31.58	30.61	97.0
38	12	2.0	35.49	34.68	100
40	12	2.0	32.75	32.72	100
45	12	2.0	33.42	33.35	100
50	12	2.0	32.87	32.42	100

At the end of the plating, the weak Ag was easily removed by simply rubbing of the surface layer with a print-board eraser, thus resulting in Ag less of 0.1–0.4 mg. Neither crater formation nor peeling off was observed during a thermal shock treatment.

The layer thickness is no longer time-controlled, but governed by the amount of Ag present in the plating bath.

### Influence of Ag quantity

Since enriched silver is expensive, the bath concentrations are held as low as practical considering the requirements of the job. In order to economize, some experiments were carried out with different silver molarities in plating solution. In this work based on the data in Table 5, it seems that the minimum amount of silver in the solution should be  $4 \text{ g}\cdot\text{l}^{-1}$  to electroplate the layer with 100% current efficiency (Table 4).



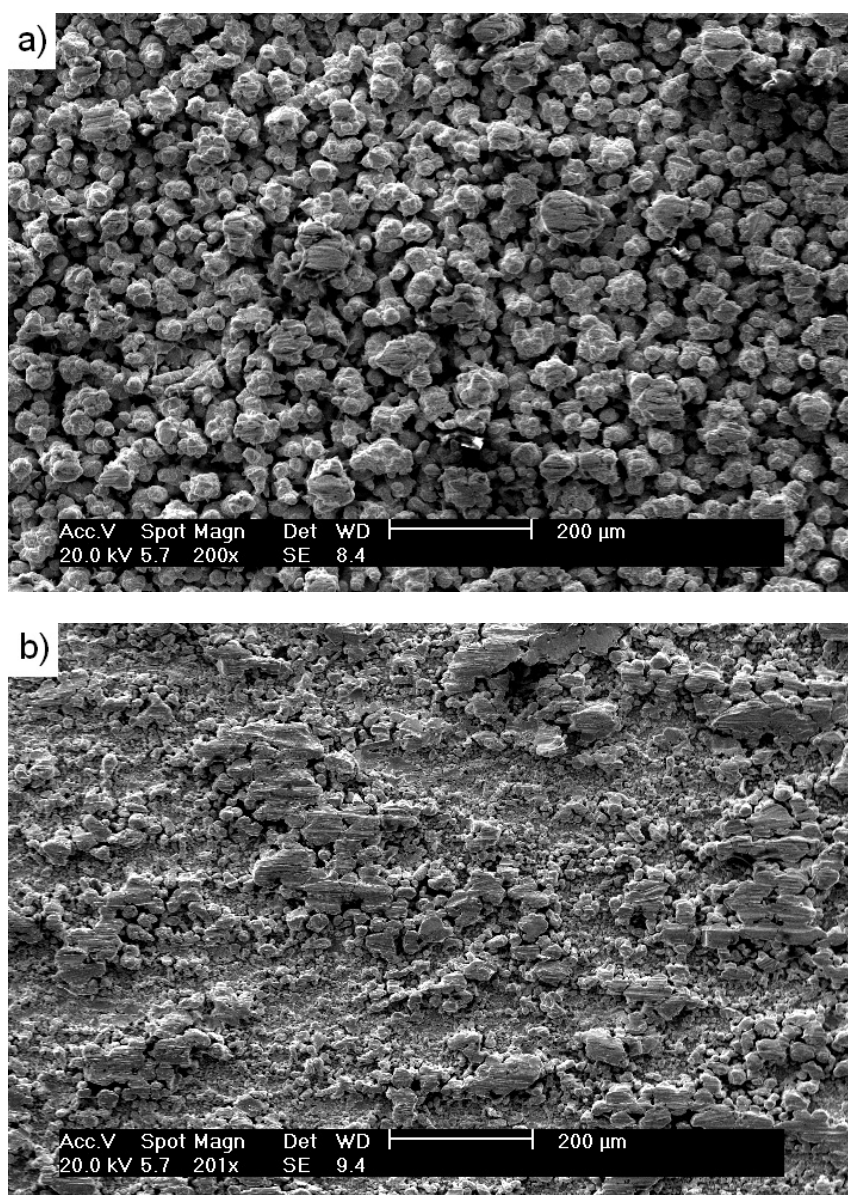
*Table 4.* Influence of silver concentration in the cyanide bath, pH 12, 2 hours, current density  $4.27 \text{ mA}\cdot\text{cm}^{-2}$ 

W(Ag), g	T, °C	$t_0$ , $\mu\text{m}$	$t_C$ , $\mu\text{m}$	Current efficiency, %
2.80	24	33.21	32.18	98.2
1.86	24	36.97	36.24	100
0.93	24	33.64	29.33	89.5*
0.93	40	28.18	27.69	84.5*
0.50	24	0.62	0.57	17.4*

\* Dull deposit was observed on the silver layer because of the quantity of silver ions in the bath. The dull deposit was easily removed by CIF cleaning and the reflective surface was obvious.

*Table 5.* Influence of electroplating time,  $5.16 \text{ g}\cdot\text{l}^{-1}$  AgCN,  $5.16 \text{ g}\cdot\text{l}^{-1}$  KCN,  $3 \text{ g}\cdot\text{l}^{-1}$   $\text{Na}_2\text{CO}_3$  solutions,  $24^\circ\text{C}$ , pH 12, current density  $4.27 \text{ mA}\cdot\text{cm}^{-2}$ 

Time, h	$t_0$ , $\mu\text{m}$	$t_C$ , $\mu\text{m}$	Current efficiency, %
2.0	37.47	36.41	100
2.5	40.92	40.85	100
3.0	49.73	49.69	
3.5	57.42	57.35	100
4.0	65.23	64.93	100
5.0	85.62	84.64	100
6.0	94.42	94.26	95.0
10.0	139.23	133.28	83.0



*Fig. 1.* SEM of a silver deposit on the Cu backing from  $8.5 \text{ g}\cdot\text{l}^{-1}$  AgCN,  $8.5 \text{ g}\cdot\text{l}^{-1}$  KCN,  $3 \text{ g}\cdot\text{l}^{-1}$   $\text{Na}_2\text{CO}_3$  solutions, pH 10,  $24^\circ\text{C}$ ,  $24 \mu\text{m}$  thickness grown at a current density of (a)  $12.82 \text{ mA}\cdot\text{cm}^{-2}$  (b)  $8.54 \text{ mA}\cdot\text{cm}^{-2}$

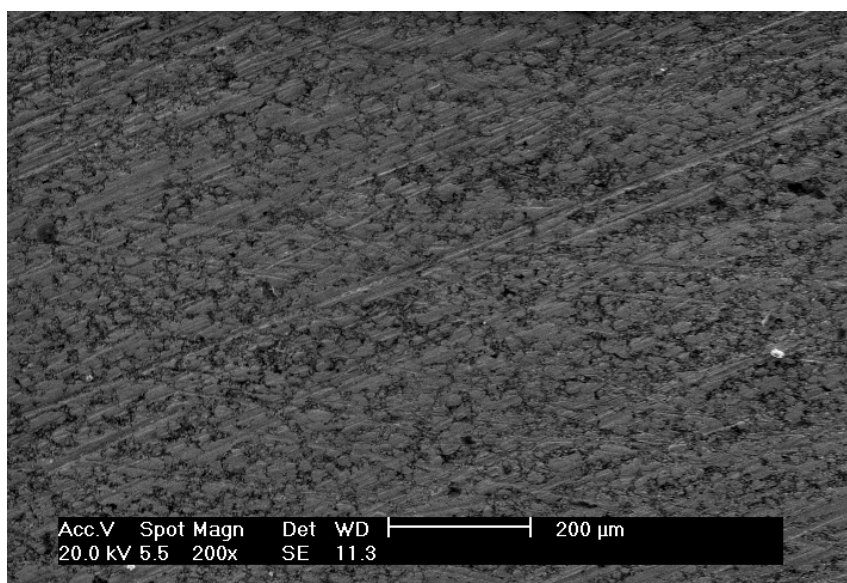


Fig. 2. SEM of a silver deposit on the Cu backing grown at a current density of  $4.27 \text{ mA}\cdot\text{cm}^{-2}$  from  $8.5 \text{ g}\cdot\text{l}^{-1}$  AgCN,  $8.5 \text{ g}\cdot\text{l}^{-1}$  KCN,  $3 \text{ g}\cdot\text{l}^{-1}$   $\text{Na}_2\text{CO}_3$  solutions, pH 8.5,  $24^\circ\text{C}$ ,  $26 \mu\text{m}$  thickness

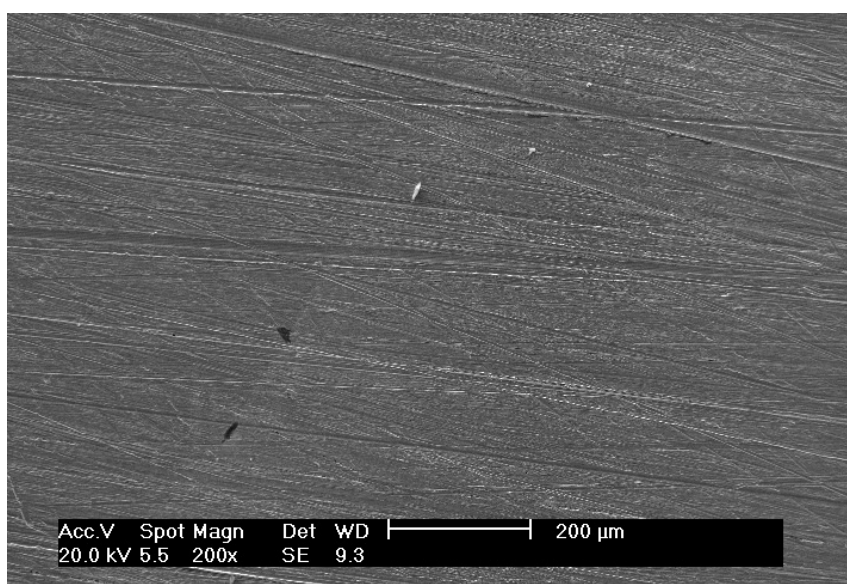


Fig. 3. SEM of a silver deposit on the Cu backing grown at a current density of  $4.27 \text{ mA}\cdot\text{cm}^{-2}$  from  $5.16 \text{ g}\cdot\text{l}^{-1}$  AgCN,  $5.16 \text{ g}\cdot\text{l}^{-1}$  KCN,  $3 \text{ g}\cdot\text{l}^{-1}$   $\text{Na}_2\text{CO}_3$  solutions, pH 12,  $24^\circ\text{C}$ ,  $133 \mu\text{m}$  thickness

### *Influence of electroplating time*

After finding the most economic and qualitative bath concentrations, some experiments were carried out for 2 to 10 hours for the solution that contained  $5.16 \text{ g}\cdot\text{l}^{-1}$  AgCN,  $5.16 \text{ g}\cdot\text{l}^{-1}$  KCN,  $3 \text{ g}\cdot\text{l}^{-1}$   $\text{Na}_2\text{CO}_3$  at  $24^\circ\text{C}$ . When the best quality and current efficiency was obtained in these experiments at room temperature and without adding any additives, a suitable molarity of the bath composition produced the current efficiency of 100% (Table 5).

### *Target quality control*

To estimate the quality of the electroplated silver targets some criteria had to be taken into account, such as homogeneity, morphology, visual appearance of the silver layer and thermal shock test.

The homogeneity of the silver layer is important as it may seriously affect the production rate of  $^{109}\text{Ca}$ . This was determined by measuring the thickness of several parts of the layer by a micrometer and calculation of the standard deviation of the data.



The morphology of all electrodeposited Ag target layers were examined by scanning electron microscopy (SEM) technique. The evaluation of quality of the layers was achieved by comparison of the photomicrographs in terms of size and form of the Ag nuclei and the extent to which they overlapped each other. The smaller, more spherical and the more overlapping nuclei were considered to be a good plating quality.

The thermal shock tests involved the heating of the target up to 500 °C for 1 hour followed by submersion of the hot target in cold (8 °C) water. Observation of neither crack formation nor peeling off of the silver layers indicated a good adhesion for the purpose.

SEM photomicrograph showed that the granulometry of electroplated targets with current density of 8.54–12.82 mA·cm<sup>-2</sup> were not as desired (Figs 1a and 1b). Hence, current density of 4.27 mA·cm<sup>-2</sup> was chosen and the SEM photomicrograph showed a suitable granulometry (Figs 2 and 3). The SEM photomicrograph of the best electrodeposition of these baths is shown in Fig. 3.

### Conclusions

$^{109}\text{Cd}$  can be produced by electroplated silver on copper backing using cyanide solution. The electrodeposition experiments were continued for complete depletion of Ag ( $\eta > 80\%$ ) with 133  $\mu\text{m}$  and optimum amount of silver (4 g·l<sup>-1</sup>) in the bath at 10 hours.

As the electrodepositions satisfy thermal shock test, current beam irradiation of higher than 200  $\mu\text{A}$  can be applied.

Ag is a precious metal and it is, therefore, essential to be recovered from the processed solution of the radiochemical separation to be re-used. The electrodeposition of Ag using cyanide baths gives quite acceptable quality for the irradiation purposes.

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