A STUDY OF THE INITIAL STAGES OF THE ELECTROCHEMICAL DEPOSITION OF THALLIUM ON COPPER – PART V
THE POTENTIAL STEP RESULTS: OVERPOTENTIAL DEPOSITION ON (111), (110) AND (100) ORIENTED COPPER SINGLE CRYSTAL ELECTRODE

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Abstract. *The overpotential deposition of thallium onto carefully chemically polished single crystal copper (111), (110) and (100) electrode from sulfate and perchlorate solutions have been investigated using single and double potential step techniques.*

It appears that the different anions used did not change the current-time response characteristics significantly. The charge corresponding to UPD monolayers of thallium ($\approx 210 \cdot 10^{-6}$ Ascm^{-2} for the first, and $\approx 400 \cdot 10^{-6}$ Ascm^{-2} for both, first and second, monolayers on all three orientations of the copper substrates used) were observed under the initial fall-off seen on the current-time transients obtained at very short times, preceding the current-time relationships for the overpotential deposition.

Indication of a rising i-t transient reflecting bulk thallium deposition on Cu(111) and Cu(100) were usually observed at $\eta = -9mV vs. Tl$, while an overpotential of $\eta = -10mV vs. Tl$ was needed for similar effects on Cu(110). The observed i vs. t^2 linearity is characteristic to 3D instantaneous nucleation and further growth of 3D centres. The results show no appreciable 3D nucleation occurring until the UPD monolayers were completed. It must be concluded, therefore, that thallium overpotential deposition on copper single crystal surfaces starts with a charge transfer controlled 3D instantaneous nucleation and proceeds by 3D growth. After some time the individual 3D centres overlap and the rate of increase of current falls off until finally the limiting current is reached. Similarly to the cases of lead deposition on Ag^{18} and Cu^{30} crystals, bulk deposition of thallium commences only after the two UPD close-packed thallium monolayers have been completed on the underlying substrate. Formation of the two UPD thallium close-packed monolayers, in the case of copper (111), (110) and (100) substrates, is an essential precursor to thicker thallium deposits; their influence on the initiation of the overpotential deposition and its growth mechanism, was shown to be very significant.

Key words: *Overpotential deposition, Potentiostatic step, Cu, Tl, Phase formation, Single crystal*

1. INTRODUCTION

The history of electrochemical metal deposition is no younger than the history of electrochemistry. It was a subject of theoretical as well as experimental research as early as 1834 [1]. Nevertheless, explanations for many of the phenomena involved are still not available. This is still particularly true for the deposition of metals on foreign substrates, where only relatively recently the phenomenon of a deposition occurring at more positive potentials than that of the bulk of the deposited metal/metal ion electrode - underpotential deposition has been closely investigated.

The knowledge gathered about metal deposition so far strongly suggests that the deposition of a metal on a similar substrate and on a dissimilar substrate, although having many features in common, does exhibit important differences. Nevertheless, an electrodeposition process could be divided basically into two parts [2-12]:

− adatom formation,
− phase formation and electrocrystallization.
    An adatom formation process includes:
a) transport of a solvated cation from the bulk of the electrolyte to the electrode/electrolyte interfacial boundary [2,9,12],
b) charge exchange between the electrode and the cation (reduction), accompanied by partial desolvation of the ion [2,3,7,13]. This provides an almost neutral and partly desolvated particle adsorbed at the electrode surface (adatom or adion) and able to move laterally over the surface.

Phase formation and electocrystallization include incorporation of adatoms (adions) into already existing crystal lattice, or their gathering together to form nuclei of a new crystal lattice [3,7,8,11-17].

In reality, these two main groups of processes are so interdependent and mixed in time that it is very difficult to separate, evaluate and follow their individual contributions to the overall process.

Despite extensive studies of metal underpotential deposition there have been some important problems still unresolved. These related principally to the nature of the monolayer (adsorbed or crystalline), the interpretation of the linear sweep voltammogram peaks, phase changes within the monolayer, the kinetics of the crystalline monolayer formation, if any, and the relevance of the UPD monolayer to the overpotential deposition process.

The system selected for the study was thallium on polycrystalline and single crystal copper electrode (surface orientation (111), (110) and (100) [19-27]). The uderpotential as well as overpotential deposition and their possible mutual interdependence were investigated. Chosen substrates posses high hydrogen evolution overvoltage and therefore hydrogen coadsorption processes do not complicate deposition of thallium.

MATERIALS AND METHODS

The experimental work described in this paper was done using single, double and triple potential pulses.

All potential programming of the working electrode was supplied either from a potentiostat ("Hi-Tek Instruments" model DT2101, or two "Chemical Electronics" models V150/1.5A, TR70/2A) in conjunction with a "Chemical Electronics" waveform generator

(type R.B.1), or two "H.Tinsley and Co." potentiometer (type 3387B). The waveform generator provided single/double potential step.

The cell currents were recorded as voltages on an XY recorder (types "Bryans 26000" or "Hewlett Packard 7015A"). In potential step experiments of longer duration, a Yt recorder ("Servoscribe 1s" RE 541.20) was used to record i-t transients. To observe and record the current-time transients and other functions too rapid to be followed on an XY or Yt recorder, oscilloscopes ("Tektronix" 547 or 5030) were employed. However, permanent records of such transients were obtained using a "Hi-Tek Instruments" signal averager (type AA1) as a transient recorder in conjunction with an XY recorder. This instrument has the ability to sample the signal-input voltage; converting it into digital form and storing it in memory having one location for each sample (256 locations). Since the time between the samples (e.g. points on an i-t curve) memorised can be altered at will, very fast transients could be reproduced from the instrument's memory on a longer time scale than used for the input of the data, thus enabling an XY recorder coupled with the signal averager to record them.

The signal averager was used in the averaging mode when i-t transients taken in the region of very small current densities (10^{-6} to 10^{-5} Acm^{-2}) showed noise levels big enough to obscure the true picture of the process. This technique relies on the fact that the time average resulting from the superposition of a number of identical signals (e.g. i-t transients) each of which has some random or periodic noise associated with it, will be the original signal but with the signal to noise ratio improved. This statement is valid provided that any periodic noise on the signal is not time locked to the repetition rate of pulsing (e.g. as would be the case if the beginning of each pulse coincided with the same point on the 50Hz mains frequency noise). On each cycle of the signal, the averager samples the signal input at fixed time intervals, converts the sampled voltages into digital form and stores the information in a memory having one location for each sample. This sampling process is repeated a pre-set number of times "n"; a trigger signal from the waveform generator ensures that samples are taken at equivalent points on each signal. Each new sample is added algebraically to the value already accumulated in the memory location, so that the final value stored is equal to "n" multiples of the average value of the sample taken at that point. If one assumes that the electrochemical process itself produces no random fluctuations in the signal level, signal content of each sample point is constant and therefore its contribution to the value stored will increase linearly with "n". However, as "n" increases, the average value of the noise will approach zero.

The overall signal to noise improvement, $(SN)_n$, is given by $(SN)_n = n^{1/2}$. Typically in the pulse experiments described here the value of "n" used was 16 or 32.

Two types of cell were used, Fig.1. and 2. The cell given in Fig.1. was used for most of the potential step experiments and was made entirely of glass. The working electrode, C, and Luggin capillary, L, were positioned in syringe barrels to enable adjustment to give the best positions and mutual distances of the two. The counter electrode, A, was either a platinum disc or a platinum mash disc ≈ 1.5 cm^2 in area, positioned parallel to the working electrode.

The cell in Fig.2. was used for potential step experiments controlled by potentiometers. This cell was also made entirely of glass. The counter electrode, A, however, was made of the metal deposited (surface area $4.5cm^{-2}$; lead "Koch-Light Laboratories Ltd.", 99.999%) and served as a reference electrode at the same time. The lead disc was pressed into a glass tube of slightly larger diameter after being wrapped with very thin ($1 \cdot 10^{-4}cm$) Teflon foil.
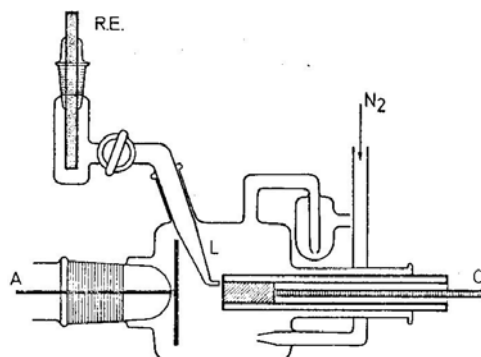
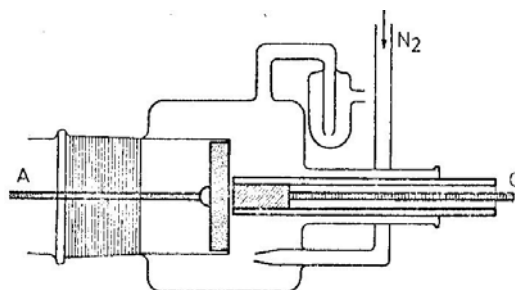Fig. 1. The cell used for most of the L.S.V. and potential step experiments.

Fig. 2. The cell used for potential step experiments on a very long timescale.

Working electrodes were small cylinders of single crystal copper ("Metal Research Ltd.", 99.999%) $\approx$ 0.8cm in diameter. These were sealed into Kel-F rod such that only the top surface of the metal cylinder was exposed to the solution. Great care was taken to ensure that no leakage occurred around the side of the metal crystal. This was achieved by cooling the cylinder of copper in liquid nitrogen before mounting in the hollow Kel-F rod (drilled for a tight fit at room temperature), which had been placed in boiling water so that insertion of the metal and contraction of the plastic housing ensured a very tight fit. Electrical contact was made via brass soldered to the copper cylinder. The reference electrodes housed at the end of the Luggin capillary were either a saturated calomel (S.C.E. "Radiometer K401") or lead wire ("Koch - Light Laboratories Ltd.", 99.999%) scaled into the glass holder.

Prior to use all glass-ware was soaked in a mixture containing equal volumes of concentrated nitric and sulphuric acids to remove any possible traces of grease, then it was rinsed thoroughly in tap water, singly distilled and finally triply distilled water. The latter was prepared by slow distillation from a weakly alkaline solution of $KMnO_4$ and then from solution containing a trace amount of ortho-H_3PO_4.

All solutions were made up from Analar grade chemicals ("B.D.H. Chemicals Ltd." and "Hopkin and Williams Company", without further purification) in triply distilled water. Prior to experiment, solutions were deaerated inside the cell by purging with a stream of purified oxygen-free nitrogen, for about 30-35 minutes. Nitrogen was purified by purging it through a

solution of ammonia metavanadate, hydrochloric acid and distilled water lying on top of $\approx$ 25g, of amalgamated zinc [28].

The importance of electrode surface preparation cannot be overstressed in connection with the metal deposition work. The surface preparation procedures finally adopted for copper single crystal electrodes were result of investigating a number of other methods. Criteria used to judge the success of each method was based on the best reproducibility of experimental data and the clearest delineation of various features on the voltammetric characteristics. The polishing process consisted of two stages, the first mechanical and the second chemical.

Firstly, the electrodes were polished on selvyt cloths ("Buchler Ltd.") impregnated with alumina ("Buchler Ltd." $5 \cdot 10^{-4}$cm and $3 \cdot 10^{-4}$cm grade, and "Banner scientific Ltd." $1 \cdot 10^{-5}$cm and $3 \cdot 10^{-5}$cm grade). Initially the largest grade was used and then progressively smaller ones down to the smallest, until the electrode had a mirror-like appearance free from scratches or blemishes. These mechanical polishing steps were always performed manually rather than on a polishing machine, which was less convenient to use. Before each experiment copper single crystal electrodes were chemically polished using a modified version of a process described elsewer [29].

The (111) oriented single crystal was immersed for 3 seconds in the acid mixture heated to over 75°C while stirring, left without stirring for another 3 seconds, then stirred and again left still for 3 seconds, finally the solution was stirred, the electrode removed and washed under a strong stream of tap water and eventually in triply distilled water. The whole procedure was repeated a second time. Then the electrode would be immersed in 30 vol.% solution of otho-phosphoric acid and stirred for 10 seconds, washed in tap water and finally with plenty of triply distilled water. If gas evolution occurred on the electrode immersed in the polishing mixture earlier than 3 seconds, then the time which the electrode spent standing still was made shorter.

The (110) oriented single crystal was immersed in the acid mixture heated to 65°C, alternately standing still and stirred every 4 seconds for 4 times. Then it was rinsed with tap water and eventually with triply distilled water. Thereafter the procedure was the same as that previously described for the (111) orientation.

The (100) oriented single crystal was immersed in the acid mixture heated to 70°C, and alternately kept still and stirred every 3 seconds four times. Then it was rinsed with tap water and eventually with triply distilled water. Thereafter the procedure was the same as that previously described for the (111) and (110) copper surface orientation.

Examinations of the polished electrode surfaces under microscope and with X-ray emission spectroscopy revealed no contaminating elements except very minute particles of alumina, but these were very few in number (on the sample investigated one particle of alumina was found in an area of about 0.25cm^2).

The amount of the copper dissolved in this chemical polishing process was relatively small. A single crystal polished several hundred times would lose 35% of its volume.

The investigation of a particular electrode solution combination always started with linear sweep voltammetry.

The voltammogram itself was a direct indication of the nature of the electrode surface and consequently could be used to assess the degree to which the polishing had been successful in producing a well-defined surface. For any particular system, repeated linear sweep experiments were performed before any additional measurements were made in order to establish an arbiter to which all future voltammetry could be referred. Potential step measurements were

made only if the linear sweep voltammetry was identical or very close to the accepted arbitrary standard, which was the clearest delineation of the voltammetric features.

The cell complete with working electrode (not yet finally mechanically polished) was rinsed thoroughly in tap, and triply distilled water. Then the cell was rinsed with the solution being used and finally filled with it. This was followed by deaeration with a rapid stream of nitrogen (scrubbed by a vanadous ion mixture) for about 35 minutes. During this process the working electrode was polarised at a potential somewhat positive to that where U.P.D. began. After the deaeration period, the working electrode was removed from the cell and finally mechanically polished as described earlier and after thorough rinsing was placed back in the cell. Gas purging was continued in the cell scaled with a syringe piston while the final mechanical polishing was performed. It was resumed for an additional 5-10 minutes after the freshly polished working electrode had been put into the cell. The process of polarising the electrode during the gas purging acted as a mild pre-electrolysis method and impurities were removed from the solution. That this was the case could be seen by carrying out voltammetry with the electrode at the end of the degassing period without chemical polishing, when markedly inferior results were obtained. Before the actual L.S.V. was recorded the cell was sealed off from the air by tight rubber covers being placed on the gas inlet and outlet.

Single and double potential steps could be applied to the working electrode, both in the UPD and the OPD regions, either by switching from channel A to channel B or on the "Hi-Tek Instruments" potentiostat (if the potential steps were of longer duration), or with the waveform generator RB1 in conjunction with a potentiostat. If the pulse train was employed, the dissolution pulse was always at least ten times the length of the deposition one, to ensure steady state conditions.

The fact that both the "Hi-Tek Instruments" potentiostat and the waveform generator had a facility for providing double step, allowed triple step experiments to be performed when the two were connected.

If potential step responses were not varying rapidly with time, the transients were recorded directly onto a Yt or XY recorder with time base supplied from the signal averager. When this was not possible, the averager was used to store and average current transients that could then be played back onto recorder.

When long duration potential step experiments in the UPD region were performed, two potentiometers with stable battery power supplies ("EXIDE" LCP13) were used to provide the working electrode with the desired potential. Potentiometers were connected to the electrode through a make-before-break switch, which enabled the choice of two pre-set potentials. The cell current was monitored with a battery driven Current picoampermeter ("Level" D.C. Multimeter type TM 9B) and recorded on a Yt recorder.

RESULTS

The bulk overpotential deposition of thallium on copper (111), (110) and (100) oriented substrates from sulphate and perchlorate solutions (10^{-1}M and 10^{-2}M Tl_2SO_4) was examined by potentiostatic methods.
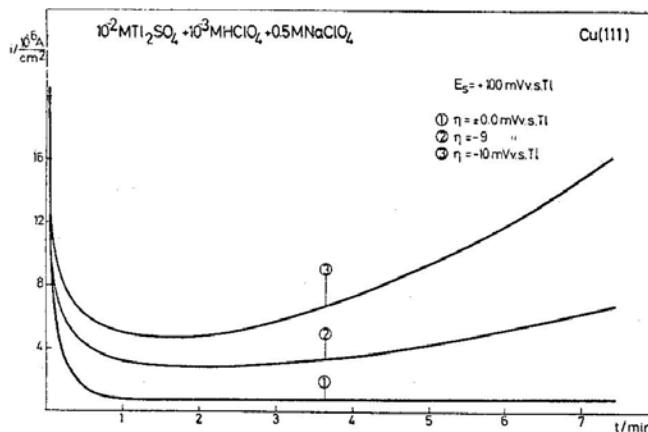
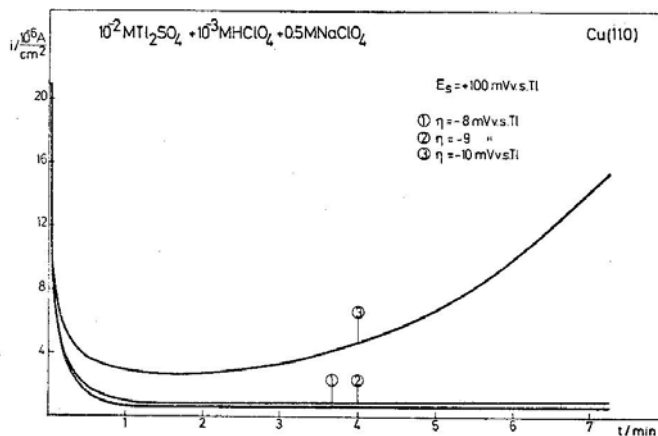Fig. 3a. Current-time transients obtained for single potential steps

Fig. 3b. Current-time transients obtained for single potential steps
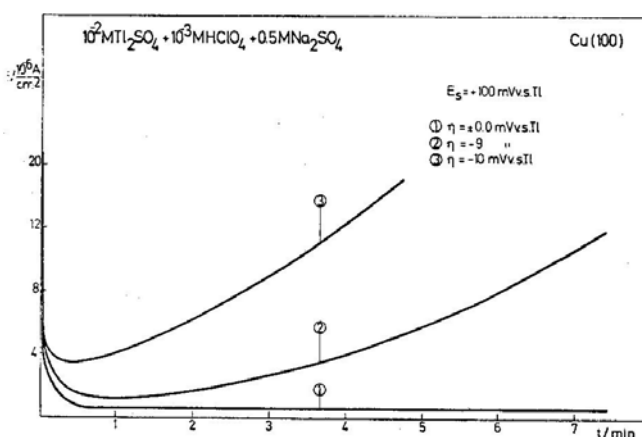
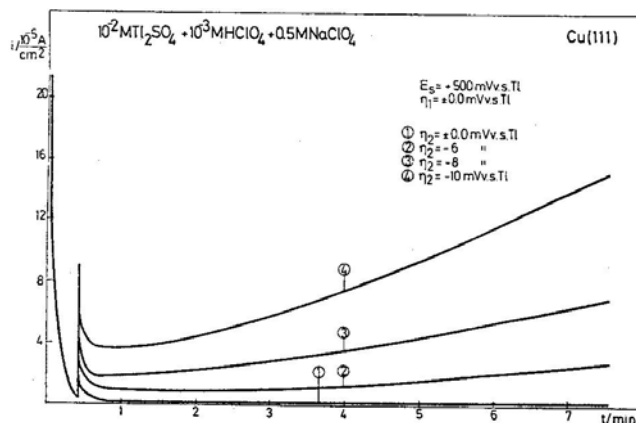Fig. 3c. Current-time transients obtained for single potential steps

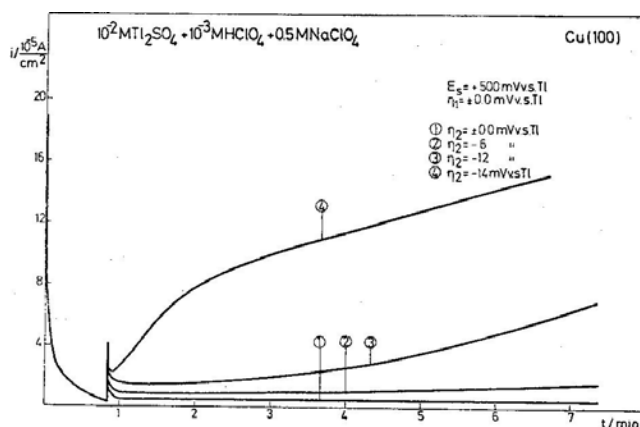Fig. 4a. Current-time transients obtained for double potential steps

Fig. 4b. Current-time transients obtained for double potential steps

Single, double and triple potential pulses were used in the way described earlier [30], except that in the present case, the starting potential, E_s, was sometimes chosen such as to correspond to potentials anodic to the second thallium UPD layer but still cathodic to the first one. Current-time responses to the single step experiments starting with E_s anodic to the second thallium UPD monolayer ($E_s = +100mV$ vs. Tl) were of the same shape, Fig. 3.a.,b. and c.

Double potential pulses starting at E_s well anodic to the first thallium UPD monolayer ($E_s = +500mV$ vs. Tl) produced bulk deposition current-time transients of a shape shown in Fig. 4.a. and b., and Fig. 5.a., b. and c.
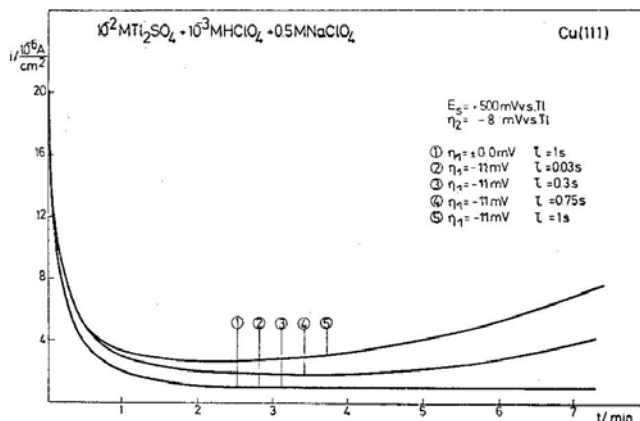
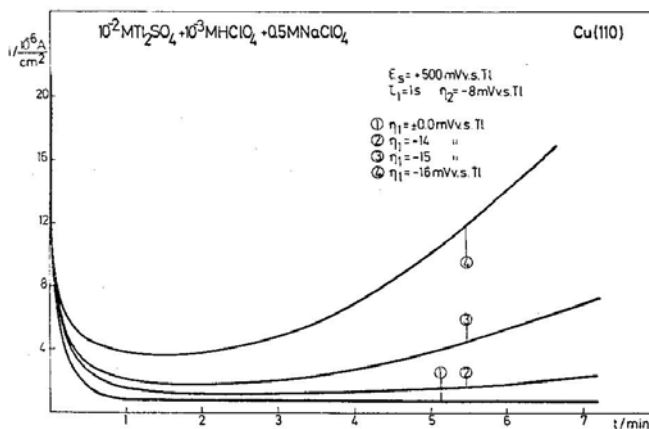Fig. 5a. Current-time transients obtained for double potential steps

Fig. 5b. Current-time transients obtained for double potential steps
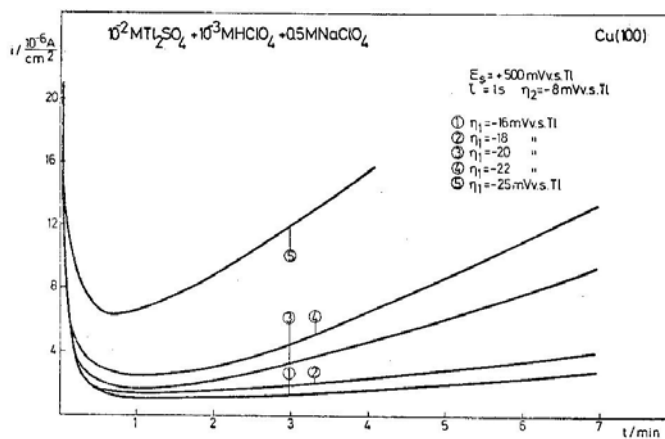
Fig. 5c Current-time transients obtained for double potential steps

DISCUSSION

Obtained results show that thallium deposition on a particular copper substrate proceeds very similarly to that observed for lead deposition [30] under the same or alike conditions.

It should be emphasised that there was no significant difference in the character of the current-time transients obtained after a UPD pre-pulse whether it started from E_s anodic to the first or to the second thallium UPD monolayer, and those obtained for pulse sequences starting at the reversible bulk potential (i.e. without UPD pre-pulse). However, the charge enclosed by the initial current fall-off with time was different in the three cases listed.

When E_s was anodic to the first UPD layer this charge was approximately $400 \cdot 10^{-6} A s cm^2$, which is in good agreement with that required for the deposition of two close-packed thallium UPD monolayers.

When E_s corresponded to a potential cathodic to the first but anodic to the second UPD layer, the charge was approximately $210 \cdot 10^{-6} A s cm^2$, and thus it corresponded most probably to the UPD of the second thallium close-packed monolayer.

No charge, even close to these values could be observed when E_s was at the thallium reversible potential (usually $\approx 40 \cdot 10^{-6} A s cm^2$).

It appears therefore that both of the UPD monolayers are always present and completed at the surface prior to bulk thallium deposition.

It should also be said that no effect due to the different thallium concentrations or the type of anions used was detected.

The dependence of thallium bulk nucleation on the overpotential applied on the three copper substrates followed the same pattern as for lead [30]; for Cu(111) and Cu(100) $\eta = -9mV$ vs.Tl/Tl$^+$ was enough to secure nucleation and further growth, while for the Cu(110) oriented surface, an overpotential of $\eta = -10mV$ vs.Tl/Tl$^+$ was needed to produce the same result, Fig. 3.a., b. and c.

Very small background currents flowing at overpotentials between $\eta = 0mV$ and $\eta = -9mV$ vs.Tl/Tl$^+$, were observed, but these did not rise during the time of observation (up to 60minutes).

It was found also, that nucleation pre-pulses of $\eta_{1(111)} = -11mV$ vs.Tl/Tl$^+$, $\eta_{1(100)} = -14mV$ vs.Tl/Tl$^+$ and $\eta_{1(110)} = -14mV$ vs.Tl/Tl$^+$, lasting for $\tau_{1(111)} = 0.75s$, $\tau_{1(100)} = \tau_{1(110)} = 1s$ were sufficient to initiate centres capable of further growth under the growth overpotentials $\eta_{2(111)} = \eta_{2(100)} = \eta_{2(110)} = -8mV$ vs.Tl/Tl$^+$, Fig. 5.a.,b.and c.

An increase in the amplitude and duration of the nucleation pulse, η_1, caused and increase in the number and size of nuclei formed during the pulse and produced an increase in the current densities at constant time during the growth pulse. A similar effect was observed when the growth pulse potential was increased.

However, the initial and subsequent shape of the i-t transients obtained did not change until overpotentials were reached when, as in the case of lead [30] deposition, the currents quickly run into planar diffusion control.

When replotted as i vs. t^2, all the initial rising portions of the current-time transients yielded linear function, Fig. 6.a., b. and c.

It must be concluded, therefore, as in the case of lead overpotential; deposition on the same copper substrate, that thallium overpotential deposition starts with a charge transfer controlled 3D instantaneous nucleation and proceeds by 3D growth. After some time the individual 3D centres overlap and the rate of increase of current falls off until finally the limiting current is reached.

Similarly to the cases of lead deposition on Ag [18] and Cu [30] crystals, bulk deposition of thallium commences only after the two UPD close-packed thallium monolayers have been completed on the underlying substrate.
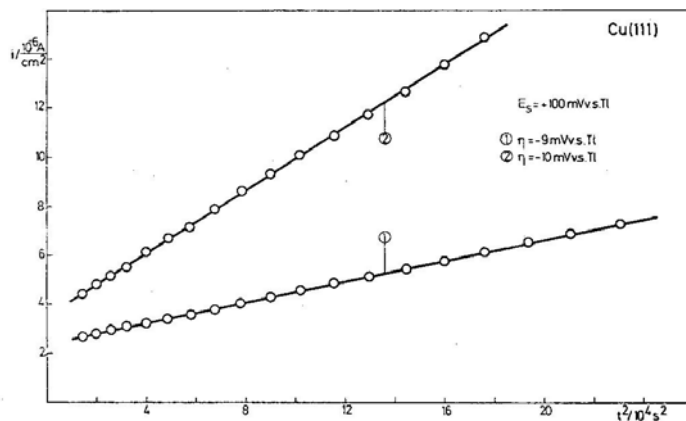
Fig. 6a. The i vs. t^2 relationships obtained from experimental data given in Fig. 3.a
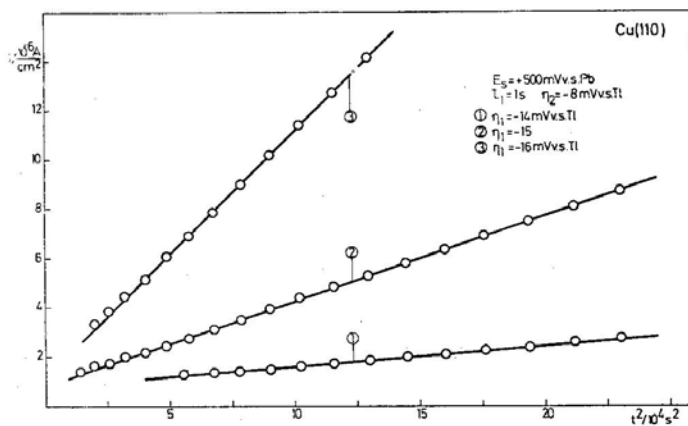

Fig. 6b. The i vs. t^2 relationships obtained from experimental data given in Fig. 5.b
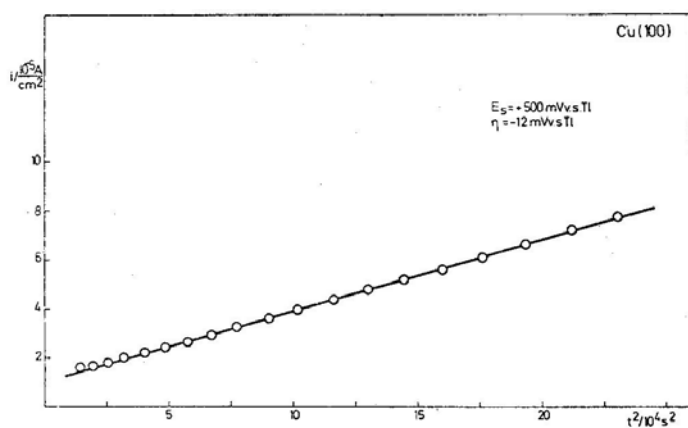

Fig. 6c. The i vs. t^2 relationships obtained from experimental data given in Fig. 5.c

The presence of the two underpotentialy deposited thallium monolayers facilitates 3D bulk thallium nucleation by changing the surface conditions, making them more favourable than they were on the original coppers ubstrate, and thus producing small nucleation overpotential. At the same time, however, they are somewhat greater than for lead on the same substrates because the two monolayers are masking nucleation active sites in the present case relatively more successfully. Although still somewhat distorted, the close-packed second UPD monolayer is a very well crystalographically defined substrate, which by comparison to the same structure on lead, most probably allows only a restricted number of orientations of nuclei to be formed which require a greater work of formation [31-39].

CONCLUSION

The results obtained by single and double potential steps into the overpotential thallium deposition region show that thallium deposition on a particular copper substrate proceeds very similarly to that observed for lead deposition [30] under the same or alike conditions.

There was no significant difference in the character of the current-time transients obtained after a UPD pre-pulse whether it started from E_s anodic to the first or to the second thallium UPD monolayer, and those obtained for pulse sequences starting at the reversible bulk potential (i.e. without UPD pre-pulse). However, the charge enclosed by the initial current fall-off with time was different in the three cases listed.

It should also be said that no effect due to the different thallium concentrations or the type of anions used was detected.

When replotted as i vs. t^2, all of the initial rising portions of the current-time transients yielded linear function.

The dependence of thallium bulk nucleation on the overpotential applied on the three copper substrates followed the following pattern; for Cu(111) and Cu(100) $\eta = -9\text{mV}$ vs.Tl/Tl^+ was enough to secure nucleation and further growth, while for the Cu(110) oriented surface, an overpotential of $\eta = -10\text{mV}$ vs.Tl/Tl^+ was needed to produce the same result.

It must be concluded, therefore, that thallium overpotential deposition starts with a charge transfer controlled 3D instantaneous nucleation and proceeds by 3D growth. After some time the individual 3D centres overlap and the rate of increase of current falls off until finally the limiting current is reached.

Similarly to the cases of lead deposition on Ag [18] and Cu [30] crystals, bulk deposition of thallium commences only after the two UPD close-packed thallium monolayers have been completed on the underlying substrate.

REFERENCES

1. M. Faraday, *Phil. Trans. Roy. Soc. London,* **124**, 77 (1834).
2. Raub, K. Muller, "Fundamentals of metal deposition", Elsevier Publishing Co., Amsterdam-New York (1967).
3. J.O'M. Bockris, A.R.Despic, Vol IX-B, Ch.7, p.p.611, "*Physical Chemistry*", ed. Eyring, Henderson, Jost, Academic Press, London-New York (1970).
4. J.A. Harrison, H.R.Thirsk, Vol.5, p.p.67, "*Electroanalytical Chemistry*", ed. A.J. Bard, Marcel Decker Inc., New York (1971).

5. M. Fleischmann, H.R. Thirsk, Vol. 3, "*Advances in electrochemistry and electrochemical engineerin*g", ed. P. Delahay, and C.W.Tobias, Interscience, London (1963).
6. A.R. Despić, A. Popov, K.: Vol. 7, "*Modern aspects of electrochemistry*", ed. J.O'M. Bockris, and B.E. Conway, Plenum Press, New York (1972).
7. B.E. Conway, J.O'M. Bockris, *Electrochim. Acta*, **3**, 340 (1966).
8. E. Budevski, *Electrochimica Metallorum*, **2,** 131(1966).
9. M. Fleischmann, S.K. Rangarajan, H.R. Thirsk, *parts I, II, III Trans.Faraday Soc*., **63,** 1241 (1967).
10. A. Sheludko, G. Bliznakov, *Izv. Bul. Academ. Nauk, Ser. Phys.,* **2,** 239 (1951).
11. T. Erdey-Gruz,"*Kinetics of electrode processes*", Adam Higher Ltd., London (1972).
12. J.O'M. Bockris, K.N. Reddy, Vol.2, "*Modern electrochemistry",* Plenum Press, Rosetta edition, New York (1970).
13. R.A. Markus, *Electrochim. Acta*, **13,** 995 (1968).
14. M. Fleischmann, H.R. Thirsk, *Electrocim. Acta*, **2**, 22 (1960), *Electrochim. Acta*, **9,** 757 (1964).
15. W.E. Garner, *Disc. Faraday* Soc., **5** (1949).
16. W.K. Burton, N. Cabrera, *Disc. Faraday* Soc., **5** (1949).
17. S.H. Bransom, W.J. Dunning, B. Millard, *Disc. Faraday* Soc., **5** (1949).
18. B. Thomas, *Ph.D. Thesis*, University of Southampton 1976.
19. J.N. Jovićević, *Ph.D. Thesis*, University of Southampton 1978.
20. A. Bewick, Jovićević, J.N., Thomas, B., Trans. *Faraday Disc.,* **12,** 24 (1977).
21. B. Thomas, A. Bewick, J. *Electroanal. Chem.*, **65,** 911 (1975).
22. B. Thomas, A. Bewick, J. *Electroanal. Chem.,* **70,** 239 (1976).
23. B. Thomas, A. Bewick, J. *Electroanal. Chem.,* **84,** 127 (1977).
24. J. N. Jovićević, A. Bewick, *Univ. Thought, Nat. Sci., Pristina,* **V(2),** 9 (1998).
25. J. N. Jovićević, A. Bewick, *Univ. Thought, Sci., Pristina,* **V(2),** 19 (1998).
26. J. N. Jovićević, A. Bewick, *Univ. Thought, Sci., Pristina,* **V(2),** 27 (1998).
27. J. N. Jovićević, A. Bewick, to be published in this journal
28. L. Meites, "*Polarographic Techniques*", 2nd edition, Interscience, New York (1965).
29. R. Pinner, *Electroplating*, 360, 401, October and November (1953).
30. J. N. Jovićević, A. Bewick, *Univ. Thought, Nat.Sci., Pristina*, **V(1),** 55 (1998).
31. N.A. Pangarov, *Phys. Stat. Sol*., **20**, 365 (1967).
32. N.A. Pangarov, *Zasht. Metalov*, **5,** 467 (1969).
33. N.A. Pangarov, *Electrichim. Acta*, **7,** 139 (1962).
34. N.A. Pangarov, *Electrochim. Acta*, **9,** 721 (1969).
35. N.A. Pangarov, S.D. Vitkova, *Electrochim. Acta*, **11**, 1733 (1966).
36. N.A. Pangarov, V. Velinov, *Electrochim. Acta*, **11**, 1753 (1966).
37. N.A. Pangarov, S.D. Vitkova, *Electrochim. Acta*, **11**, 1719 (1966).
38. N.A. Pangarov, L.A. Uvarov, A.T. Vagramyan, *Electrochim. Acta,* **13,** 1905 (1968).

STUDIJA POČETNOG STADIJUMA ELEKTROTALOŽENJA TALIJUMA NA BAKRU – V DIO
REZULTATI DOBIJENI POTENCIOSTATSKIM PULSEVIMA: ELEKTROTALOŽENJE PRI KATODNIM PRENAPETOSTIMA NA BAKARNOJ MONOKRISTALNOJ POVRŠINI KRISTALOGRAFSKE ORIJENTACIJE (111), (110) I (100)

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Ovo je peti iz serije radova u kojima se iznose rezultati istraživanja početnih stadijuma elektrotaloženja talijuma (iz sulfatnih i perhloratnih rastvora) na polikristalnom i monokristalnom bakru. Rad predstavlja rezultate dobijene potenciostatskom metodom jednostrukog i dvostrukog pulsa na monokristalnim bakarnim elektrodama površinske kristalografske orijentacije (111), (110) i (100) u području potencijala negativnijih od reverzibilnog potencijala (katodna prenapetost) talijuma u datoj sredini. Karakteristike odgovora struje-vreme na primenjene režime potenciostatskih pulseva nisu se značajnije razlikovale s obzirom na različite anjone u izabranim rastvorima.

Početni opadajući dio i-t krive (odražavajući $\approx 210 \cdot 10^{-6} Ascm^{-2}$ za prvi talijumov monosloj ili $\approx 400 \cdot 10^{-6} Ascm^{-2}$ za zbir oba talijumova monosloja, zavisno od uslova taloženja, za sve tri kristalografske orijentacije upotrebljenih bakarnih podloga) redovna je predhodnica naknadnim djelovima i-t krive koji odražavaju elektrotaloženje olova pri katodnoj prenapetosti.

Rastuće i-t krive, koje odražavaju elektrotaloženje masivnog talijuma na Cu(111) i Cu(100) podlozi javljaju se već pri katodnim prenapetostima od $\eta = -9mV vs.Tl$, a na Cu(110) podlozi pri $\eta = -10mV$ vs.Tl.

Zapažena linearnost funkcija i = f (t^2) karakteristična je za trodimenzionu trenutnu nukleaciju i dalji rast stvorenih centara. Dobijeni rezultati ne pokazuju da dolazi do značajnije trodimenzione nukleacije talijuma prije nego što se predhodno u potpunosti ne formiraju dva monosloja talijuma. Činjenica da je nukleaciona prenapetost olova na ispitivanim bakarnim povr{inama ($\eta_{(111)} \leq \eta_{(100)} \leq \eta_{(110)}$) tako mala mora biti rezultat uticaja tih monoslojeva.

Kako su monoslojevi talijuma dobijeni pri potencijalima pozitivnijim od reverzibilnog po karakteru kristalne (metalu slične strukture) po osobinama bliže talijumu (posebno drugi talijumov monosloj) nego bakru, njihovo prisustvo neminovno mijenja površinske uslove u pravcu smanjivanja slobodne energije trodimenzione nukleacije. Do promjene slobodne površinske energije trodimenzione nukleacije dolazi najvećim dijelom na granici faza nukleus-talijumov monosloj i kao posljedicu ima smanjenje potrebnog rada formiranja 3D nukleusa. Ovo smanjenje rada potrebnog za formiranje nukleusa, nadalje je olakšano i postojanjem poremećene strukture epitaksijalnog gustopakovanog monosloja, što omogućava veći izbor mogućih kristalografskih orijentacija nukleusa (hkl) koji se formiraju.

Formiranje monosloja olova pri potencijalima pozitivnijim od reverzibilnoga, u slučaju Cu(111), Cu(110) i Cu(100) podloge predstavlja neophodnu i nezaobilaznu predhodnicu debljim talijumovim talozima, a njihov uticaj na započinjanje i mehanizam rasta talijuma pri potencijalima negativnijim o reverzibilnog pokazao se značajnim.