JOURNAL OF APPLIED ELECTROCHEMISTRY 5 (1975) 151–154

Study of electrodeposition on moving wires by potentiostatic pulses

A. TVARUSKO*

Engineering Research Center, Western Electric Co, Princeton, N. J. 08540

Received 21 August 1974

Current density-time curves were measured at various cathodic potentiostatic pulses of short duration ($\leqslant 0{\cdot}1$ s) on stationary and moving horizontal copper wires of 0·51 mm diameter in 0·24 M $CuSO_4$ – 2·36 M H_2SO_4 solution. The magnitudes and the shapes of the $I-t$ curves were greatly influenced by the wire speeds. The limiting current densities from these transients, ${}_EI_L$, are higher and increase with wire speed at a smaller rate than the potentiodynamic I_L. The role of uncompensated IR–drop is discussed.

1. Introduction

The current density-potential curves and the limiting current densities, I_L, were obtained earlier by linearly varying the cathode potential on stationary [1] and moving [2] wires. The $I-V$ curves can also be constructed from the current densities measured at the end of long or short potentiostatic pulses [3].

This paper describes the current density-time, t, curves at various cathodic potentiostatic pulses of short duration on stationary and moving horizontal copper wires of 0·51 mm diameter in an overflow cell [4] and compares the resulting $I-V$ curves and I_L values with those obtained potentiodynamically.

2. Experimental

The experimental wire electroplating setup and its modification were described earlier [1,4]. The experiments were made at 22·0 ± 0·2°C in flowing $CuSO_4$ solutions with large excess of H_2SO_4. The current density values reported here are all mean values averaged over the entire wire surface.

3. Results and discussion

The time dependence of the cathodic current density during potentiostatic pulses of -750 mV was shown earlier to illustrate the efficacy of the experimental setup [4]. During these short (50 ms) pulses the wire makes less than one half revolution (0·43) even at the highest wire speed used (33·2 m s^{-1}), i.e., only unplated clean wire is used in these experiments [2]. The current density decreased with time on stationary wires in the absence or presence of fluid flow in the overflow cell. On the other hand, I remained nearly constant on wires moving above 6 m s^{-1} [4]. This is in apparent disagreement with the potentiodynamic results described elsewhere [2]. Before discussing the reasons for this, let us see the $I-t$ behaviour at different applied voltages during longer pulses.

Fig. 1 shows the time dependence of the cathodic current density for various potentiostatic pulses of 100 ms duration for a stationary wire. The applied cathodic voltages are given as positive values in this and other $I-t$ curves. In every case, the cathodic current density increases very rapidly (<1 ms) to a maximum from which it decreases with time. The magnitude of the current density at the end of the pulse increases with increasing applied potential except in the range $\sim -0{\cdot}6$ to $\sim -0{\cdot}9$ V, i.e., on the I_L plateau

---

*Present address: Laboratoire Suisse de Recherches Horlogères, CH – 2000 Neuchâtel, Switzerland.

where I remains practically constant. At higher cathodic potentials, I starts to increase again due to the discharge of H^+ (often no H_2 bubbles are observed [5]).

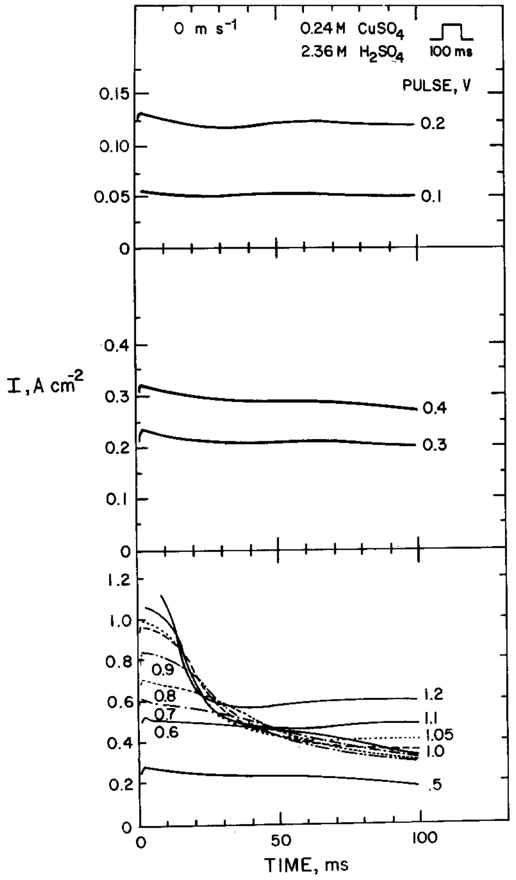

Fig. 1. Current density as a function of time at various cathodic potentiostatic pulses of 100 ms duration. The wire is stationary and the solution is 0·24 M $CuSO_4$–2·36 M H_2SO_4 flowing at 6 l min^{-1}.

The behaviour of I in the initial part of the pulse depends on the magnitude of the applied voltage. The magnitude of the initial part of the curve increases with increasing voltage near and on the I_L plateau whereas I at the end of the pulse remains practically constant. However, above the I_L plateau, i.e., during simultaneous metal deposition and H^+ discharge, I increases at both places and the initial peak becomes narrower. Since most of the practical electrodeposition takes place below I_L, i.e., maximum electrodeposition rate without the detrimental H_2 evolution, the initial current-time behaviour near and above I_L was not pursued any further.

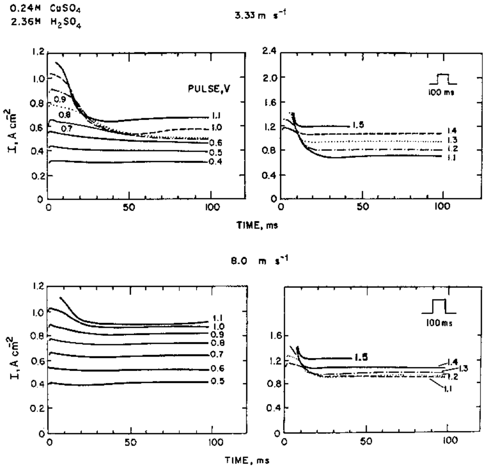

Fig. 2. Time dependence of current density during various potentiostatic pulses of 100 ms duration. The wire is moving at 3·3 and 8·0 m s^{-1}. The 0·24 M $CuSO_4$ — 2·36 M H_2SO_4 solution flows at 6 l min^{-1}.

Fig. 2 shows the time dependence of current density at various applied voltages on wires moving at 3·3 and 8·0 m s^{-1}. A cursory inspection of the I—t curves (Figs. 1 and 2) already reveals the effect of the wire movement. The magnitude of I increases with increasing wire speed. For example, I at the end of the —0·5 V pulse at 3·3 ms^{-1} wire speed is double that on a stationary wire. Further increase of the wire speed does not seem to alter the magnitude of I_L at this applied voltage.

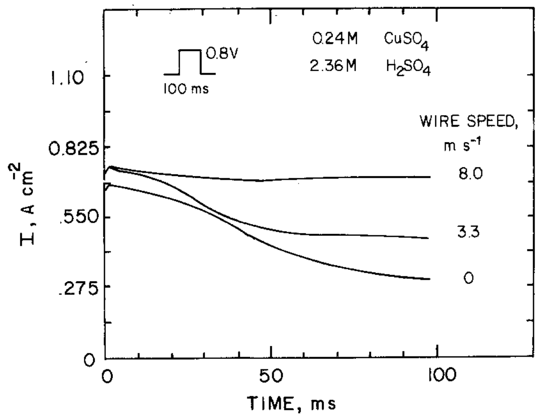

Fig. 3. Current density as a function of time at —0·8 V potentiostatic pulses of 100 ms duration on wires moving at various speeds. The 0·24 M $CuSO_4$ — 2·36 M H_2SO_4 solution flows at 6 l min^{-1}.

Let us take a higher applied voltage, —0·8 V, which is near the centre of the I_L plateau on a stationary wire. These $I-t$ curves are plotted in Fig. 3 for greater clarity and to make the visual comparison easier. The current density at the end of the potentiostatic pulse markedly increases with wire speed. The decrease of I with time is greatly affected by the wire speed and becomes smaller as the wire speed increases and the current changes only by a small amount at 8 m s^{-1}. The current decrease is due to the well-known fact that the initial deposition rate cannot be maintained because of the presence of kinetic and, especially, mass transfer limitations [6]. The increased fluid velocity near the moving wire increases the mass transfer rate and, thus, a higher current density can be maintained [1,2,7]. This, however, seems to be complicated by the continuously entering fresh wire surface [2] which is suddenly subjected to the cathodic potential. Thus, the current density on this new segment will suddenly increase as if a pulse were applied. During the wire's travel through the cell, the local current density at this point will decrease to a value which depends on the fluid velocities in the vicinity of the wire. The higher the wire speed, the higher the fluid velocity will be in the vicinity of the moving wire, i.e., the less the current density will decrease. The fluid flow due to the wire movement seems to be the dominating factor. It is very tempting to assign the small increase of I starting at ∿ 50 ms on the 8 m s^{-1} $I-t$ curve (Fig. 3) to the continuously entering fresh wire surface, especially in view of the time (57·2 ms) needed to completely replace the wire originally present in the cell.

Some of the features of the $I-t$ curves can be seen more clearly in their corresponding $I_E - V$ curves. Fig. 4 shows the current density (I_L), measured at the end of a given 100 ms wide potentiostatic pulse as a function of the applied voltage, i.e., the transient $I-V$ curves; these $I_E - V$ curves are similar to the potentiodynamic ones [4]. It can be seen that the limiting current density, ${}_{E}I_L$ increases with increasing wire speed. A comparison of the two $I-V$ curves reveals that the potentiodynamic $I-V$ curves have inherently more detail. The $I_E - V$ curve at 13·3 m s^{-1} did not reach the ${}_{E}I_L$ plateau in this concentrated solution because the required current was above the capability of the potentiostat (10 A). This is one reason for using more dilute solutions; the other is the lower IR–drop.

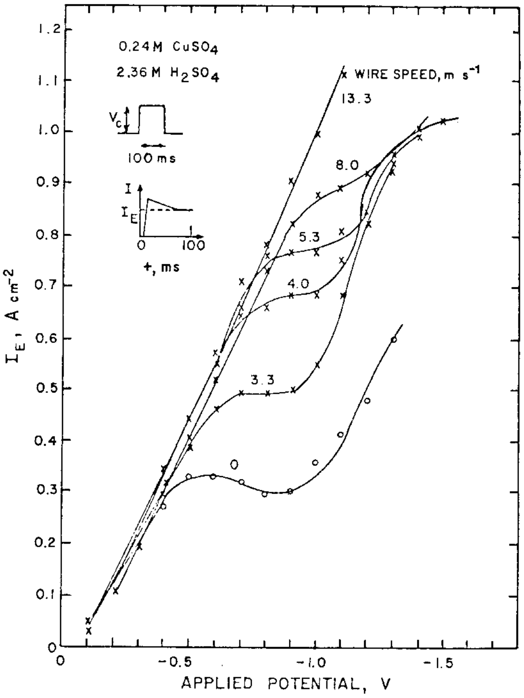

Fig. 4. $I_E - V$ curves obtained from potentiostatic pulse measurements on wire moving at various speeds. The 0·24 M $CuSO_4$–2·36 M H_2SO_4 solution flows at 6 l min^{-1}.

The limiting current densities of the transient $I-V$ curves, ${}_{E}I_L$, (Fig. 4) are significantly higher than the I_L values obtained from potentiodynamic $I-V$ curves [2] and have a larger spread. The ${}_{E}I_L$ – wire speed correlation is given by: $\log {}_{E}I_L = -0{\cdot}60 + 0{\cdot}64 \log V_m$ (coefficient of correlation, $R = 0{\cdot}934$), where V_m is expressed in m s^{-1}. The slope of this regression line is considerably lower than the 0·90 of the corresponding $I_L - V_m$ regression line (Table 1 in reference [2]). This is due to the fact that the current density during these transients does not have sufficient time to reach a steady state especially at lower wire speeds. At higher wire speeds, the decrease of I is small due to the beneficial effect of fluid flow generated by the wire movement.

It was shown earlier [4] and mentioned briefly in this paper that the current density at the end of a given potentiostatic pulse increased to a certain wire speed. Above this wire speed, I remained constant in disagreement with the potentiodynamic results [2].

The reason for this can be explained on the basis of the $I_E - V$ curves in Fig. 4. The magnitude of the applied voltage was −0·75 V in the previously published $I-t$ curves [4]. This is in the middle of the $_EI_L$ plateau at zero wire speed (Fig. 4). Once the wire moves above approximately 5 m s^{-1}, the change of current density is practically negligible [4] because the I_E values fall on the rising part of the $I_E - V$ curves and are not influenced by the wire speed. The $_EI_L$ plateau, however, is present at higher potential values. This shift is due to the uncompensated IR−drop in the solution near an equipotential wire surface. The interpretation of the $I-t$ curves on non-equipotential wire surfaces is more complex and was described elsewhere]8].

In view of the aforementioned, it is obvious that wrong mass transfer rate conclusions can be reached if one chooses a certain potential for the current density measurements under different transient or steady-state conditions and does not consult the $I_E - V$ curves. The potentiodynamic $I-V$ curves are more advantageous for mass transfer rate measurements because they are easily and directly obtained in less time and the correct I_L values can be extracted even in the absence of automatic IR−drop compensation. These results were described earlier [2]. On the other hand, the potentiostatic pulses yield some information which is not easily or not at all available from the potentiodynamic $I-V$ curves such as kinetic parameters, mechanisms of electrocrystallization, adsorption and surface coverage by organic species, and oxide formation.

Acknowledgement

The author wishes to thank Mr W. E. Wilson, Jr for his valuable experimental assistance.

References

[1] A. Tvarusko, Electrodepos. *Surface Treat.* **2** (1974) 481.
[2] A. Tvarusko, *Electrochim. Acta,* accepted for publication.
[3] A. Tvarusko, *Plating* **61** (1974) 139.
[4] A. Tvarusko, *J. Electrochem. Soc.* **119** (1972) 43.
[5] A. Tvarusko and L. S. Watkins, *ibid.* **118** (1971) 580.
[6] K. J. Vetter, "Elektrochemische Kinetik", Springer-Verlag, Berlin (1961).
[7] A. Tvarusko, *Plating* **60** (1973) 345.
[8] R. C. Alkire and A. Tvarusko, *J. Electrochem. Soc.* **119** (1972) 340.