Facts and Fiction about Pulse Plating

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SUMMARY — This paper illustrates some of the basic principles of pulse plating and examines the effect of pulsed current on the current density distribution, limiting current density, rate of deposition and power consumption. Some specific examples of the effect of pulsed current on various deposit properties have been considered. Emphasis has been placed on what may be expected to be achieved in practical situations and the practical limitations of the pulse plating process have been discussed in terms of maximum practical frequency and minimum practical duty cycle.

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INTRODUCTION

The aim of this paper is to examine some of the facts and myths concerning pulse plating. The use of modulated current has been employed for many years and it is well known that the use of periodic reverse (P.R.) plating can improve the throwing power of cyanide copper plating electrolytes under certain conditions[1]. During the development of pulse plating, some incredible claims have been made for the benefits which can be obtained by the use of pulsed current. It has been stated that maximum deposition rates can be increased by several orders of magnitude and that power savings can be realised by the use of pulsed current[2]. Some Russian workers have claimed that deposition rates could be increased indefinitely provided that short enough pulses were used[3]. Other claims include improved throwing power, reduced porosity, increased hardness and better ductility. It is intended to examine some of these claims and try to give some indication of what may be expected in practice from a commercially available pulse plating unit.

CHARACTERISATION OF PULSED CURRENT

Before the effect of pulsed current on various aspects of metal deposition is considered, it is necessary to examine the way in which pulsed current waveforms are characterised.The advent of modern electronics and microprocessor control has permitted great flexibility over the programming of the applied waveform. Trains of pulses can be programmed to give very complex waveforms. Square waves are the easiest waveforms to produce because this requires only a switching arrangement rather than a specialised waveform generator[4]. Current waveforsms can be divided into two major groups; these are unipolar pulses where all the pulses are in one direction, and bipolar pulses where anodic and cathodic pulses are mixed. There are many variants on these groups, but as the complexity of the waveform increases, so the number of variables increases which makes it difficult to understand how a particular waveform affects the electrodeposition process. Consequently, the present discussion will be restricted to the consideration of the simplest case of unipolar and bipolar pulses, i.e. pulse and pulse reverse.

In order to characterise a direct current, it is sufficient to know the current density. The characterisation of a train of current

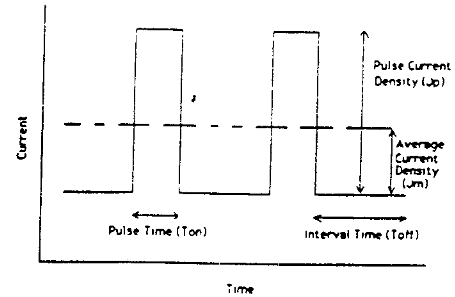

Figure 1. Characterisation of Unipolar Pulses.

pulses requires three parameters to be known[5]. These are the pulse current density, the pulse length and the interval between the pulses as shown in Figure 1.

$$j_m = \frac{j_p \cdot t_{on}}{(t_{on} + t_{off})} \quad (1)$$

A quantity frequently encountered is the duty cycle; this represents the percentage time in each cycle when the current is on and is defined by the following equation:

$$\text{Duty Cycle (\%)} = \frac{t_{on} \cdot 100}{(t_{on} + t_{off})} \quad (2)$$

The product of the duty cycle and the pulse current density gives the average current density. The characterisation of a pulsed reverse current waveform requires four parameters to be known and is defined by the following equation:

$$j_m = \frac{j_c \cdot t_c + j_a \cdot t_a}{(t_c + t_a)} \quad (3)$$

Where:

j_c = Cathodic pulse current density
j_a = Anodic pulse current denstiy
t_c = Cathodic pulse time
t_a = Anodic pulse time

It should be noted that the peak current densities (j_c and j_a) are of opposite sign.

LIMITATIONS IMPOSED BY DUTY CYCLE AND FREQUENCY

The average current density is very important as it defines the rate of metal deposition and is equivalent to the applied current density in direct current plating. Here, the first major limitation of pulse plating from a practical viewpoint becomes evident. In order to produce the same average deposition rate as for direct current, as duty cycle is reduced, so the pulse current density needs to be increased. For example, at a duty cycle of 10%, a

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pulse current density of 40 A/dm^2 is required for an average current density of 4 A/dm^2. In practical applications, this would seldom be viable due to limitations of rectifier capacity. Some researchers have quoted interesting effects of pulsed current using duty cycles as low as 0.1%[6] but this would require a pulse current density of 4000 A/dm^2 to produce an average current density of 4 A/dm^2 which is clearly impractical. As duty cycle is increased, it begins to approach direct current so a compromise situation needs to be achieved. If sufficient spare rectifier capacity is available, a duty cycle of 33-50% is probably the minimum practical value. For applications using high current, such as chromium plating, a value of 50-75% would be the lowest usable duty cycle.

After considering the practical limitations of duty cycle, it is necessary to consider the effects of frequency which is defined as the reciprocal of the cycle time. Some manufacturers of pulse plating equipment advocate the use of very high frequencies but the practical maximum frequency which can be applied to a plating electrolyte is limited by the capacitance of the double layer at the interface between the plating electrolyte and the article being plated [7-10]. This arises due to a charge separation at this interface and gives rise to high capacitance; a value of 50 $\mu F/cm^2$ is not uncommon. The net effect is that the cathode behaves as a resistor and a capacitance connected in parallel. When a pulse is applied to the system, some of the applied current is used to charge this capacitance to the applied potential. This current is not lost but is recovered at the end of a pulse when the double layer discharges. If the frequency is very high, the double layer does not fully charge during the pulse or fully discharge during the off time. This has a smoothing effect on the applied waveform which begins to approach direct current and so limits the maximum useful frequency to around 500 Hz for most applications. However, higher frequencies can be used where very high pulse current densities are employed because the double layer charge and discharge times become shorter as pulse current density is increased.

THE EFFECT OF PULSED CURRENT ON CURRENT DENSITY DISTRIBUTION

Primary current density distribution depends only upon the cell geometry and is independent of electrochemical parameters, thus the primary current density distribution would be unaffected by the applied current waveform. The primary current distribution is modified in plating solutions by the secondary current density distribution which arises due to the effects of activation overpotential. Because the resistance of the cathode surface is much less than that of the electrolyte, the cathode can be considered to be an equipotential surface and this tends to counteract the effect of irregular geometry and to equalise the current density distribution. In general, the greater the rate of change of potential with increasing current density, the more the overall current density distribution tends towards a secondary distribution and, excluding mass transport effects, produces a more even metal distribution. As current density is increased, the electrode resistance falls so the rate of change of potential with current density also becomes less. Thus as current density is increased, so the current distribution tends towards a primary distribution and the throwing power usually deteriorates. In electrolytes where metal ions are not strongly complexed and cathodic efficiency is high, a low current density usually produces a better throwing power than a high current density. With any form of modulated current, whatever the shape of the waveform and whether unipolar or bipolar pulses are used, in order to maintain the same rate of deposition as for direct current, the cathodic current density during the cathodic pulse must be higher than the equivalent direct current density. This means that the overall current density distribution tends towards a primary distribution when pulse plating is employed[6,11]. Consequently, the deposit distribution would be expected to be less uniform using pulsed current than with direct current.

In electrolytes where the cathodic efficiency is less than 100%, the use of pulsed current may change the relative efficiencies of metal deposition and hydrogen discharge and may under suitable conditions produce an increase in throwing power.

Electrolytes containing organic additives may undergo changes in the deposition mechanism when pulsed current is used which can produce changes in the uniformity of deposition which have a beneficial effect on throwing power. Recent research work studying the effects of pulsed reverse current[12,13] on the electrodeposition of copper from acid electrolytes containing a combination of a polyether, a sulphopropyl sulphide and chloride ions has shown that substantial improvements in "hole throwing power" can be achieved when these electrolytes are used for the deposition of copper on printed circuit boards. This has been shown to be due to the effects of pulsed reverse current on the adsorption characteristics of the sulphopropyl sulphide[12]. The net effect of this is that holes become depolarised relative to the surface of the boards which can result in preferential deposition in the holes. This represents a very useful practical application of the use of pulsed current and is an area of research which has up to now been unexploited. Potentially, there may be many more applications of the use of pulsed current to influence the effects of organic addition agents.

THE EFFECT OF PULSED CURRENT ON THE MAXIMUM RATE OF DEPOSITION

Claims have been made that pulse plating can improve the maximum rate of deposition obtainable from a plating electrolyte by several orders of magnitude[3]. The theory behind this reasoning is that as frequency is increased, the diffusion layer becomes thinner. However, the diffusion system which is encountered with pulse plating is as shown in Figure 2[11,14]. If pulses of a high frequency are applied to a plating system, the diffusion layer does not have time to disperse completely between pulses and so the diffusion system consists of a stationary layer where the concentration gradient depends on the average current density applied, and a pulsating layer where the concentration gradient varies with time[11]. The total thickness of the diffusion layer is equivalent to that obtained when plating with direct current. Because of this, the use of pulsed current has very little effect on the limiting current density. Metal ions cannot be discharged faster than they are supplied to the cathode surface. The rate of supply of metal ions depends only on hydrodynamic and concentration factors and is little influenced by the applied waveform.

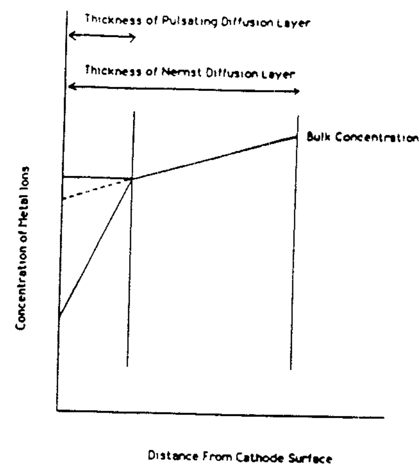


Figure 2. A simplified illustration of the diffusion system obtained when current pulses are applied to a plating electrolyte.

The major factors governing the supply of metal ions to the cathode surface are the rate of agitation (and other hydrodynamic factors i.e. viscosity and diffusion coefficients) and the metal ion concentration. The rate of usage of metal ions depends only on the average current density and is not influenced by the shape of the waveform. However, having stated that pulse plating cannot increase the limiting current density of a plating electrolyte, it must be considered that the maximum current density at which a plating electrolyte can be practically operated is usually only 10 to 20% of the theoretical limiting current density. This is because mass transport effects produce "burning" at higher current densities. Clearly, there is room for improvement and it has been claimed that higher plating rates can sometimes be achieved with pulsed current due to improved deposit properties. This effect is attributed to the effect of pulsed current on the process of electrocrystallisation rather than an enhancement of the rate of mass transport.

THE EFFECT OF PULSED CURRENT ON POWER CONSUMPTION

As already stated, to maintain the same average rate of deposition as for direct current, a higher current density has to be employed during the pulses. This causes the

electrode resistance to fall which means that the average cathode potential for a given current density is lower for pulse plating than for direct current as shown in Figure 3.

This has led some workers to claim that savings in power consumption can be made by the use of pulsed current[2]. Unfortunately, average cathode potential cannot be used for power calculations since the rectifier has to supply enough voltage to give the peak cathode potential which is higher for pulse plating applications than for direct current as shown in Figure 4. Data for the plotting of Figures 3 and 4 were obtained by substituting published values of exchange current density into the Volmer-Butler equation (equation 4) and calculating peak and average overpotentials assuming no flattening or mass transfer limitations. A value of 0.5 was assumed for α.

$$j_f = j_o \left[\exp\left(\frac{\alpha z F \eta_a}{RT}\right) - \exp - \left(\frac{(1-\alpha) z F \eta_a}{RT}\right) \right] \qquad (4)$$

Where:-

- α = Transfer coefficient.
- z = Ionic charge of discharging species.
- F = Faraday constant.
- R = Gas constant.
- T = Temperature (K).
- η_a = Activation overpotential.
- j_f = Faradaic current density.
- j_o = Exchange current density.

Thus when pulsed current is used, a higher cell voltage is required to give an equivalent current density. Because power consumed is the product of the cell voltage and the applied current, the power consumption is always greater for pulsed current than for direct current. The extra power consumed can cut down heating bills for plating solutions but may cause overheating problems, particularly when low duty cycles are used in high power applications.

THE EFFECT OF PULSED CURRENT ON DEPOSIT PROPERTIES

Pulsed current has the ability to affect the mechanisms of electrocrystallisation which control the physical and mechanical properties of the electrodeposited metal. For example, the nucleation rate of a growing electrodeposit is proportional to the applied current density, thus the use of high current density current pulses can produce deposits with reduced porosity, and in some cases a finer grain size. Whether a finer grained deposit is obtained in practice depends upon what happens when the current is interrupted because this can allow the desorption of impurities from the growing deposit which encourages grain growth rather than the formation of new grains[15]. The effects which are obtained in practice are thus dependent on the specific electrochemical system to which the current pulses are applied.

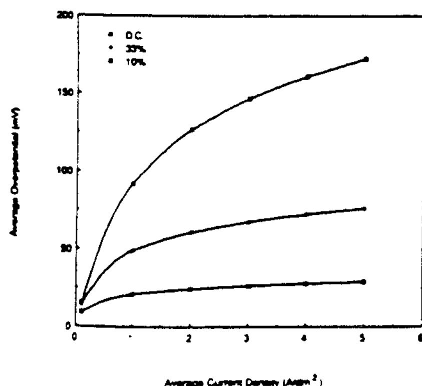


Figure 3. Average overpotential vs average current density for a silver cyanide plating electrolyte.

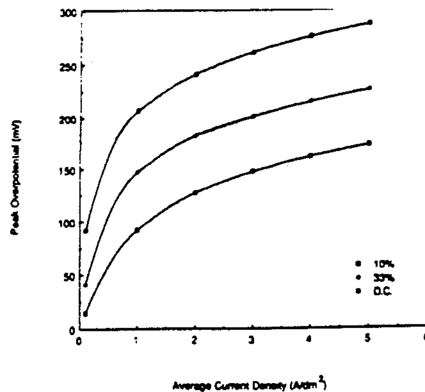


Figure 4. Peak overpotential vs average current density for a silver cyanide plating electrolyte.

A good example of grain growth caused by the desorption of impurities is observed when current pulses are applied to acid gold/cobalt alloy plating electrolytes[16]. In this case, deposits by pulsed current have a very low carbon and nitrogen content and as can be seen from Table 1, the grain size is increased. There is also a significant increase in the ductility of these deposits and an increase in density and electrical conductivity.

Table 1. Grain sizes of gold deposits from a citrate buffered gold/cobalt alloy plating electrolyte (after Fluhman et. al.[16]).

Deposits produced at an average current density of 1 A/dm².

Plating Conditions	Grain Size (A)	Comments
Direct Current.	250	Many inclusions in deposit. Twinning present but no dislocations.
Pulsed Current. 10 ms on, 20 ms off	500	Inclusion density approx. half that obtained with D.C. Twinning more pronounced than with D.C.
Pulsed Current. 10 ms on, 100 ms off	1000	No inclusions in deposit. Twinning very pronounced. Dislocations present.

Unfortunately, the impurity content of acid gold electrolytes is important when the gold deposits are to be used for contact applications because the codeposited polymer acts as a lubricant and prevents galling and cold welding of the contacting surfaces[17-20]. Thus pulse plated gold deposits often give poorer performance in contact applications in spite of the higher purity of the deposit and improved electrical properties.

A large amount of research work has been carried out studying the influence of pulsed current on the properties of electrodeposited metals and it is not possible to cover all of these in this review. However, a few examples are highlighted which have been studied in our research programme. One of the metals which was selected for possible investigation was nickel which was of interest because of the claims of the ability of pulsed current to control the levels of stress in nickel deposits[21,22]. This has some obvious applications in the electroforming industry where stress control is of paramount importance. A spiral contractometer was used to measure the mean stress of deposits from a Watt's electrolyte using direct current and unipolar pulses at various duty cycles while holding the average current density constant in order to maintain equivalent deposition rates. The results obtained are shown in Figure 5.

It can be seen from this figure that the effect of pulsed current was to move the stress in a tensile direction and that the level of tensile stress changed in an approximately linear fashion with decreasing duty cycle. It can also be seen that the effect is much less at a higher frequency. This is an example of the smoothing effect of the double layer capacitance as described earlier. In practical situations, a stress of close to zero is required and so increasing the level of tensile stress is unlikely to be very useful. Some work was attempted using sulphamate based electrolytes but the results were not very representative of practical situations because of a beaker scale, when a realistic current density was applied to the contractometer spiral, anode passivity caused the oxidation of sulphamate which resulted in a high level of compressive stress in the deposits[23,24]

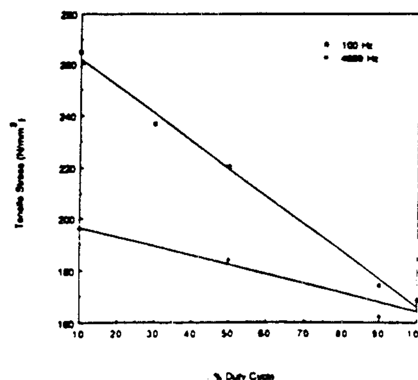


Figure 5. Tensile stress vs % duty cycle at 100 and 4999 Hz

Values quoted represent the mean stress after 20 minutes plating time at an average current density of 4 A/dm²

deposits, the effect of pulsed current was to move the stress in a tensile direction. It was discovered that the only way to obtain a substantial reduction in the level of tensile stress in Watt's electrolytes was to use pulsed reverse current. Reductions in level of tensile stress of nickel deposits from a chloride based electrolyte have been noted by Kendrick[25] which is in agreement with the experimental results obtained for the Watt's electrolyte.

The effect of unipolar pulses on the internal stress of deposits of chromium from a sulphate catalysed electrolyte was also studied. In this case the level of tensile stress in the deposits is reduced by the use of current pulses as can be seen from Figures 6 and 7. This reduction in stress enables the production of crack free deposits of chromium[26-28]. Crack free chromium can be produced from certain high temperature electrolytes using direct current[29] but the deposits obtained from these electrolytes are relatively soft. By using pulsed current, with high frequencies, it is possible to produce chromium deposits of up to 1000 Hv as can be seen from Figure 8. For certain applications, these deposits may give enhanced corrosion protection although the chromium layer is very brittle and deformation of the substrate material

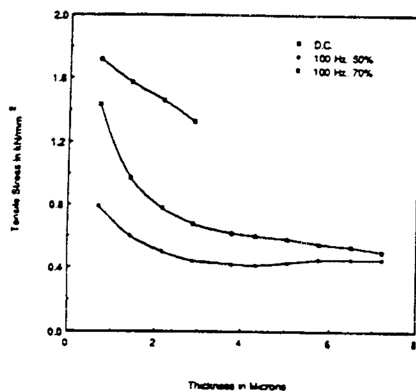
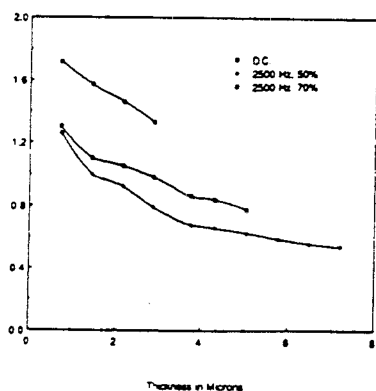


Figure 6. Tensile stress vs coating thickness for chromium deposits from a sulphate catalysed electrolyte at a pulse frequency of 100 Hz.



ure 7. Tensile stress vs coating thickness for omium deposits from a sulphate catalysed trolyte at a pulse frequency of 2500 Hz

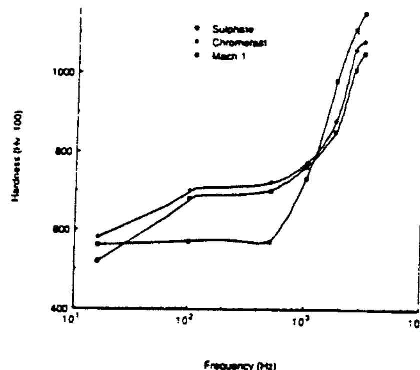


Figure 8. Hardness vs pulse frequency at 50% duty cycle of deposits from three different chromium plating electrolytes at an average current density of 40 A/dm².

(Chromefast C and Mach 1 are commercial plating electrolytes from W. Canning Ltd.)

will cause macro cracking of the deposit. The use of pulsed reverse current has also been shown to produce crack free chromium deposits[30-32].

There are many reported effects of pulsed current on the properties of electrodeposited metals but these are specific to each electrochemical system studied and it is not possible to generalise. The examples quoted serve to illustrate this specific nature.

CONCLUSIONS

1. The use of modulated current with electrochemical systems where metal ions are not complexed and cathodic efficiency is high would generally be expected to produce less uniform metal distribution than direct current. In cases where cathodic efficiency is significantly less than 100% or where organic additives are used, beneficial effects are obtained in some cases.
2. The use of pulsed reverse current for the electrodeposition of copper from acidic electrolytes containing a suitable combination of organic additives (polyethers and sulphopropyl sulphides) produces enhanced throwing power due to a change in the electrolyte polarisation characteristics caused by the influence of the pulsed reverse current on the adsorption characteristics of the additives. This application has proved to be very useful in improving the "hole throwing power" of electrolytes used for the production of printed circuit boards.
3. The limiting current density for a plating electrolyte cannot exceed that for direct current when modulated current is used under equivalent hydrodynamic conditions. In isolated cases, faster practical deposition rates may be obtained by using pulsed current due to improved deposit properties.
4. Power consumption is always increased by the use of pulsed current because a higher cell voltage is always required for an equivalent rate of deposition as compared to direct current.
5. Deposit properties can be affected significantly by the use of pulsed current. These effects are specific to the electrochemical system to which the current pulses are applied so it is not possible to generalise. However, it can be stated that when the practical limitations of duty cycle and frequency are taken into consideration, the effects of pulsed current on deposit grain size are usually small in comparison to the effects of organic additives.

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