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CURRENT EFFICIENCY AND ELECTROCHEMICAL EQUIVALENT IN AN ELECTROLYTIC PROCESS

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ABSTRACT

Calculations of current efficiency of an electrolytic reaction and of electrochemical equivalent of the metal involved are discussed. A formula for the electrochemical equivalent of a ternary alloy is also given.

The current efficiency of an electrolytic process is that percentage of total quantity of electricity consumed, which is effectively utilised for the desired electrolytic reaction. In metal deposition, for example, the conditions of bath operation, like temperature and current density are so chosen that the current efficiency is high without the desirable properties of the deposit being deleteriously affected. A high current efficiency is desirable for any cathodic or anodic process for, only then can one be sure of the reaction concerned, proceeding unimpeded.

In cases where only a single metal is involved, the current efficiency can be determined from relevant data with a simple formula as below :

Current efficiency = Mass of metal deposited or dissolved × 100 (per cent)

> ampere seconds electrochemical equi-(coulombs) of × valent of the metal electricity consumed

An extension of this formula to electrolytic alloy deposition or dissolution leads one to conclude that summing up of the individual current efficiencies is necessary. The formula for current efficiency of alloy deposition is given by

$$\frac{P_1M_0}{e_1|T} + \frac{P_2M_0}{e_2|T}$$

where P_1 and P_2 are the percentages by mass M_a of the alloy deposit, e_1 and e_2 the respective electrochemical equivalents and I, the current passed for a duration of T seconds, is of great help in determination of the current efficiency of a binary alloy [1].

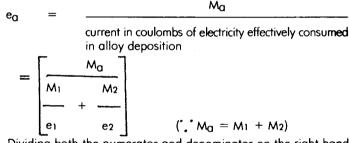
It is well known that the electrochemical equivalent should be taken into account for calculation of the current efficiency. The formula for electrochemical equivalent

$$e_0 = \frac{e_1 e_2}{e_1 f_2 + e_2 f_1}$$

where e_1 and e_2 are the individual electrochemical equivalents of binary alloy constituents and f_1 and f_2 are fractions by mass, was reported to be applicable to binary alloy deposition with 100 per cent current efficiency [2]. A close examination of the factors involved shows, however, that the electrochemical equivalent of an alloy is not connected with the current efficiency though it should be useful for determination of the latter. How can one calculate the electrochemical equivalent of a binary or even a ternary alloy and hence the overall current efficiency for its electrolytic deposition or dissolution is shown in the following paragraphs.

Let M_a be the mass of the binary alloy deposited under certain conditions. If it is assumed that e_a is the electrochemical equivalent

of the alloy, e1 and e2 those of the constituent metals, and M1 and M2 their masses making up the deposit,



Dividing both the numerator and denominator on the right hand side by $M_{\mbox{a}},$

$$e_{0} = \left[\frac{1}{\frac{1}{M_{0}}\left(\frac{M_{1}}{e_{1}} + \frac{M_{2}}{e_{2}}\right)}\right]$$
$$= \left[\frac{1}{\frac{1}{e_{1}} \cdot \frac{M_{1}}{M_{0}} + \frac{1}{e_{2}} \cdot \frac{M_{2}}{M_{0}}}\right]$$
$$= \left[\frac{1}{\frac{f_{1}}{f_{1}} + \frac{f_{2}}{f_{2}}}\right] \text{ (f1 and f2, fractions by}$$
$$= \frac{e_{1}}{f_{1}e_{2}} + \frac{e_{2}}{f_{2}e_{1}}$$

Now only a simple calculation is required for determining the current efficiency of binary alloy deposition.

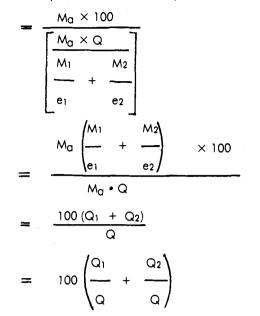
$$M_{a} \times 100$$

mass)

Current efficiency (%)

 $e_a \times coulombs$ of electricity passed

Natarajan — Current efficiency and electrochemical equivalent in an electrolytic process



If P1 and P2 are percentages by mass of each alloy constituent and Q is taken as IT,

 $= \begin{bmatrix} P_1 M_0 & P_2 M_0 \\ \hline \\ e_1 \cdot IT & e_2 \cdot IT \end{bmatrix}$ current efficiency (%)

which is the same as referred to earlier.

The formula for the electrochemical equivalent of a ternary alloy can also be derived. If M1, M2 and M3 are the masses of the alloy constituents and e1, e2 and e3 their electrochemical equivalents respectively,

$$e_{d} = \frac{M_{d}}{M_{1} \qquad M_{2} \qquad M_{3}}$$
$$\frac{M_{1}}{M_{1}} + \frac{M_{2}}{M_{1}} + \frac{M_{3}}{M_{3}}$$
$$\frac{H_{1}}{H_{1}} + \frac{H_{2}}{H_{2}} + \frac{H_{3}}{H_{3}}$$

$$= \frac{1}{\frac{1}{M_{a}} \begin{pmatrix} M_{1} & M_{2} & M_{3} \\ \hline & + & - & + & - \\ M_{a} \begin{pmatrix} e_{1} & e_{2} & e_{3} \end{pmatrix}}$$

$$= \frac{1}{\begin{pmatrix} M_1 & 1 \\ \dots & \dots \end{pmatrix}} + \begin{pmatrix} M_2 & 1 \\ \dots & \dots \end{pmatrix}} + \begin{pmatrix} M_3 & 1 \\ \dots & \dots \end{pmatrix}} + \begin{pmatrix} M_3 & 1 \\ \dots & \dots \end{pmatrix}} + \begin{pmatrix} M_3 & 0 \\ \dots & 0 \end{pmatrix}}$$

$$= \frac{f_1}{f_1} + \frac{f_2}{f_2} + \frac{f_3}{f_3}$$

$$= \frac{e_1 \cdot e_2 \cdot e_3}{f_{1223} + f_{223e1} + f_{321e2}}$$

$$M_a \times 100$$

e_a × coulombs of electricity passed

of

$$= \frac{M_{a} \times 100}{\begin{pmatrix} M_{a} \times Q \\ M_{1} & M_{2} & M_{3} \\ e_{1} & e_{2} & e_{3} \end{pmatrix}}$$

$$= \frac{M_{a} \begin{pmatrix} M_{1} & M_{2} & M_{3} \\ e_{1} & e_{2} & e_{3} \end{pmatrix}}{M_{a} \cdot Q} \times 100$$

$$= \frac{100 (Q_{1} + Q_{2} + Q_{3})}{M_{a} \cdot Q} \quad (Q_{1}, Q_{2}, Q_{3} \text{ coulombs of electricity consumed})$$

$$\begin{pmatrix} Q \\ 100 \\ - + - + - + - + - \end{pmatrix}$$

Q.

If P1, P2 and P3 are the percentages by mass of each alloy constituent, and Q is taken as IT,

Q

١Q

Current efficiency (%)	=	1	P2Ma	· · ·
		eılT	e2IT	e₃IT
		[MI	M2 +	Мз Т
	=	1 .		
		eılT	e₂IT	e3IT

The current efficiency is thus equal to the sum of the individual current efficiencies.

REFERENCES

- 1. A. Brenner, 'Electrodeposition of Alloys', Vol. I, New York, Academic Press (1963), p.149
- 2. F.A. Lowenheim (Ed), 'Modern Electroplating', New York, Third Edition, John Wiley & Sons, Inc. (1974), p.502.

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