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SHORT COMMUNICATION

Evidence for anodization kinetics of molybdenum as a valve metal in buffer solutions of pH 9.3

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1. Introduction

The confusion regarding the anodization kinetics of molybdenum under constant current conditions [1–3] was recently clarified as a result of our intensive studies [4]. The charging curves of molybdenum in strong acid solutions were found to be similar to those of valve metals. In weak acid, neutral and alkaline solutions, there was an induction period before the oxide fomation [3, 4]. Although Ikonopisov [3] claimed that the anodization kinetics of molybdenum were appreciably different from those of valve metals, our previous investigation in strong acid solutions showed that Ikonopisov's conclusion was not accurate. Oxidation of molybdenum in strong acid solutions under constant current follows the familiar Güntherschulze and Betz relationship [5]:

$$i = A \exp^{BH} \qquad (1)$$

where i is the anodic current density, H is the electric field strength and A and B are the electrolytic parameters. The field strength, $H = (\mathrm{d}E/\mathrm{d}x)_i$ where E is the electrode potential and x is the oxide film thickness. The field strength, electrolytic parameters and other kinetic parameters were found to be comparable with those for valve metals. Also, the electrical breakdown during anodization of molybdenum showed many characteristics of valve metals [6]. It has become accepted that the anodization of molybdenum covers the metal with an insulating film of MoO_2 [7–10]. The stability of the anodic oxide film on molybdenum in aqueous solutions was recently tested [11]. It was found that the film is capacitative, insulating and very resistant to corrosion.

Owing to the change in efficiency of oxide formation during the anodization of molybdenum in non-acid solutions, coulometry cannot be used to estimate the oxide film thickness and, instead, capacitance measurements were used. The increase of the oxide film thickness, dx, was calculated by using the following relation [12, 13];

$$\mathrm{d}x\,(\mathrm{cm}) = \frac{Da \times 1.11 \times 10^{-6}}{4\pi}\,\mathrm{d}C_m^{-1} \qquad (2)$$

where C_m is the measured capacitance in μF, a is the apparent surface area in cm^2 and D is the dimensionless dielectric constant. Assuming that $D = 29.4$ [14], the field strength can be determined as [4, 15, 16];

$$H_i(\mathrm{V\,cm^{-1}}) = \frac{4\pi}{Da \times 1.11 \times 10^{-6}}\,(\mathrm{d}E/\mathrm{d}C_m^{-1})_i \qquad (3)$$

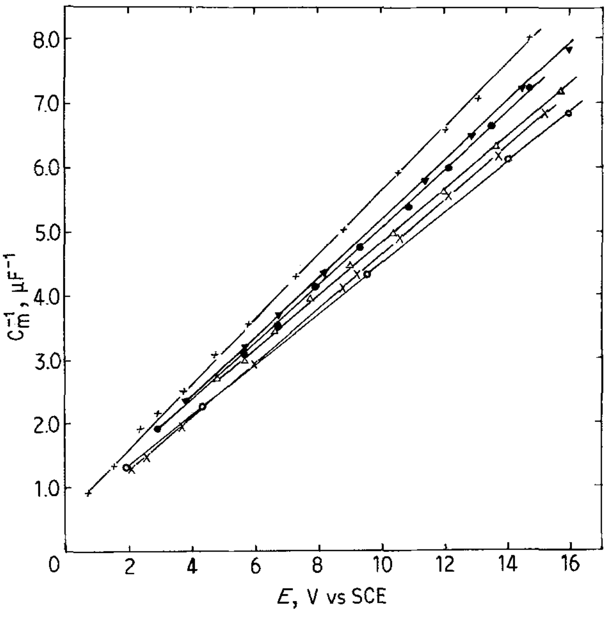

Fig. 1. Variation of reciprocal capacitance with formation voltage during anodization of spec. pure molybdenum electrode (Johnson-Matthey, England) in modified universal buffer solution of pH 9.3 at c.d.s of: (+) 50; (▽) 100; (●) 200; (△) 700; (x) 1200 and (○) 1600 μA cm^{-2}; area = 0.125 cm^2 and temperature = 30° C.

2. Experimental results

The experimental details were the same as those described previously [4, 15]. The variation of C_m^{-1} with formation voltage, E, during anodization of

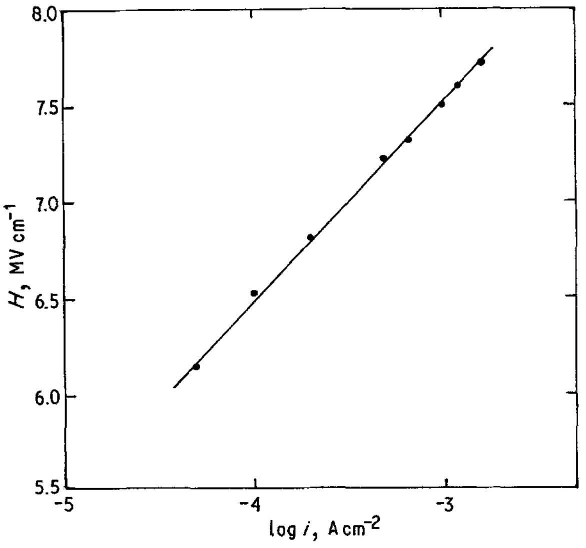

Fig. 2. Electric field strength versus logarithm of anodizing current density.

Table 1. Electric field strength, as estimated from capacitance measurements, during anodization of molybdenum at 1 mA cm^{-2} in 0.2 M salt solutions of different anions

Solution	H, V cm^{-1}
NaF	7.50 × 10^6
NaCl	6.83
NaBr	6.83
Na_2SO_4	7.32
$NaNO_3$	7.50
$NaHCO_3$	7.15
$Na_2B_4O_7$	7.69
$NaNO_2$	6.03
KH_2PO_4	7.50
K_2HPO_4	7.60
$K_2Cr_2O_7$	7.69
Sodium oxalate	7.69
Sodium citrate	7.50
Sodium formate	5.91
Sodium acetate	6.15
Sodium benzoate	6.03
Sodium salicylate	6.15
Potassium tartrate	7.79
Potassium hydrogen phthalate	5.70

molybdenum in modified universal buffer solution (Britton and Robinson [17]) of pH 9.3 at different c.ds. is shown in Fig. 1. Using equation (3), the field strength was estimated from Fig. 1 as a function of the anodizing c.d. Taking the logarithm of both sides of equation (1) yields;

$$\log i = \log A + BH \qquad (4)$$

The validity of equation (1) can be seen in Fig. 2. Additionally, the field strengths associated with the oxide film formation, as determined from capacitance measurements, are listed in Table 1. The values of field strength are comparable with those of valve metals under similar conditions and also their extent of variation with the anion type [15, 16]. No sequence for the dependence of the field strength on the anion type can be deduced.

In conclusion, molybdenum anodizes in aqueous media at constant current density with the formation of an insulating oxide film of changeable formation efficiency, following the familiar Güntherschulze and Betz relationship.

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