

ROLE OF ZIRCONIUM ON THE DISSOLUTION AND DEPOSITION OF COPPER FROM SULPHURIC ACID SOLUTIONS

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Copper containing zirconium alloys found extensive applications in aerospace and cryogenic applications because of its superior mechanical properties at elevated temperatures as well as for low temperature applications. The rapid solidification technique produced copper containing 0.5% zirconium to offer high strength and conductivity. Zirconium cannot be deposited by electrochemical methods as its deposition potentials are too negative and zirconium has low hydrogen over voltage. The present investigation aims at the role of zirconium sulphate on the deposition and dissolution of copper from sulphuric acid solutions.

Keywords: Zirconium alloy and solidification technique

INTRODUCTION

Copper containing zirconium alloys found extensive applications in aerospace and cryogenic application [1-4]. The rapid solidification technique was used to obtain copper with 0.5% Zr alloy [5]. This alloy exhibited high strength and conductivity. The electrolytic extrusions methods was used to identify the phases in Cu-0.63, Zr-0.4, Cr - 0.59 Al and Cu-0.18 Zr alloys and the Cu₅Zr was found to cause higher electrical conductivity [6]. Zirconium cannot be deposited by electrochemical methods as its deposition potentials are too negative and zirconium has low hydrogen over voltage. Attempts to deposit Cu-0.1 Zr alloy on foreign substrates are few.

This paper presents the deposition of Cu-Zr alloy on brass and the role of Zr on the electrochemical behaviour of copper in H₂SO₄ solutions.

EXPERIMENTAL

Brass specimens [10 x 10 x 1 cm] were polished and degreased by using trichloroethylene. The plating bath consists of 0.8 M CuSO₄, 0.75 M H₂SO₄ and 0.013 to 0.05 M ZrSO₄. The deposition was carried out at 2.4 A.dm⁻² using OFHC copper anodes. The hardness was measured using LECO micro hardness tester by applying a load of 50 g; The wear resistance was measured by using

Erichser Taber Abrasion Tester Model 503 (W Germany).

Cyclic voltammetric experiments were carried out in a single compartment three electrodes cell assembly. A platinum miniature electrode (0.25 cm²) and a large platinum foil (6.25 cm²) were used as working and counter electrodes respectively. The working electrode potentials were monitored using a saturated calomel electrode as reference electrode. Cyclic polarization was carried out using Bio Analytical systems (USA) Model 100 A. All solutions were prepared using analar chemicals. Various concentrations of CuSO₄ and ZrSO₄ ($1.25 \times 10^{-2} < x > 5 \times 10^{-2}$ MM) solutions were used. Experiments were carried out at 303 ± 0.1 K.

RESULTS AND DISCUSSIONS

Physicochemical studies

The hardness of the electrodeposited Cu-Zr alloys (Table I) revealed that with increase of Zr content in the alloy Vicker's hardness is also increased. The wear resistance of the Cu-Zr alloy deposits were followed under a load of 1 Kg for 1000 cycles. The wear index of the alloy decreased with Zr content thereby indicating the Zr additions favour wear resistance (Table II).

TABLE I: Effect of zirconium on the hardness of the copper deposit

Concn of zirconium (M)	Vicker's hardness (VHN)
0	80.8
0.013	84.8
0.026	86.5
0.039	101.0
0.050	115.0

Cyclic voltammetric studies

Fig. 1 presents the cyclic voltammogram in 0.04 M CuSO₄ containing 0.038 M sulphuric acid solutions. When polarized from +600 mV to -500 mV, the forward scan exhibited a peak at -136 mV which become more negative with sweep rates. The hydrogen evolution was found to occur beyond -350 mV. During the reverse scan, an anodic peak appeared at -193 mV which become more active with sweep rate.

Introduction of zirconium sulphate to the solution did not affect the electrochemical spectrum (Fig. 2). The cathodic peak potentials became more negative with zirconium sulphate concentration suggesting that the reduction of copper ions was hindered by the presence of zirconium sulphate.

The electrochemical behaviour of copper is determined by its nobility with respect to most other metals and the existing divalent copper ions in solutions. The standard reduction potential Cu²⁺ ions is 100 mV Vs SCE and the reversible potentials 60 mV Vs SCE in 4 x 10⁻² M CuSO₄ solution [7-8]. Earlier polarographic studies on copper (II) solutions containing complexing agents revealed two polarographic waves corresponding to step wise reduction of copper [9]. Under transient polarization condition (5-100 mV/sec) the deposition of copper may involve the formation of monovalent copper [10].

TABLE II: Effect of zirconium on the wear resistance of the copper deposit

Concn of zirconium (M)	Wear index (Kg/1000 cycles)
0	0.083
0.013	0.076
0.026	0.074
0.039	0.073
0.050	0.071



If step (1) is slow,

$$I_c = k_1 [\text{Cu}^{2+}] \exp -\beta F \frac{\Delta \phi}{RT} \quad (3)$$

where $\Delta \phi$ is the interfacial potential difference; β is the symmetry factor.

A slow second electron transfer under Langmuir would give

$$I_c = k_2 k_1 (\text{Cu}^{2+}) \exp(1 - \beta) F \frac{\Delta \phi}{RT} \quad (4)$$

For an irreversible process,

$$E_{p,c} = E^0 - \frac{RT}{\alpha_c} F \left[0.78 + \ln \left(\frac{D_0}{K_0} \right)^{1/2} + \ln \left(\frac{\alpha_c F}{RT} \right)^{0.5} \right] \quad (5)$$

where K_0 is the standard rate constant; E^0 is the formal potential of the electrode [$dE_{p,c}/d \log v$] would give a slope of $(2.303 RT/\alpha_c F)$. The observed value of 60 mV/decade suggests that, a non Langmuir behaviour.

Under non activated Temkin conditions for slow step (1),

$$I_c = k_1 [\text{Cu}^{2+}] \exp -\frac{\beta F \Delta \phi}{RT} \exp(1 - \beta) \frac{r_0 F}{RT} \quad (6)$$

$$\text{and } I_a = k_2 [\text{Cu}] \exp(1 - \beta) \frac{F \Delta \phi}{RT} \exp -\frac{\beta \theta r F}{RT} \quad (7)$$

where θ is the surface coverage and r is the interaction parameter. This would result [$dE_{p,c}/d \log v$] = 60 mV/decade.

Influence of zirconium sulphate addition

Addition of zirconium sulphate in solution did not markedly affect the cathodic peak potential

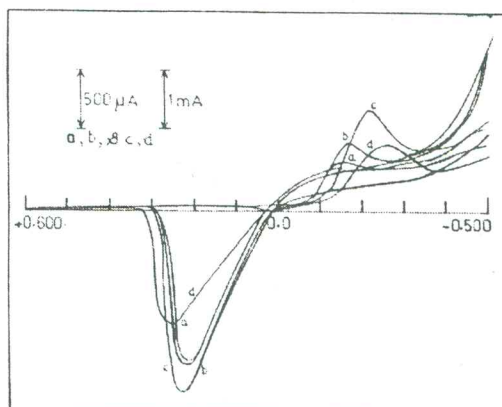


Fig. 1: Typical cyclic voltammogram in 0.04 M H₂SO₄ at different sweep rates
 a = 5 mV/sec (b) = 10 mV/sec (c) = 25 mV/sec
 (d) = 50 mV/sec $E_{\lambda a} = +600$ mV $E_{\lambda c} = -500$ mV

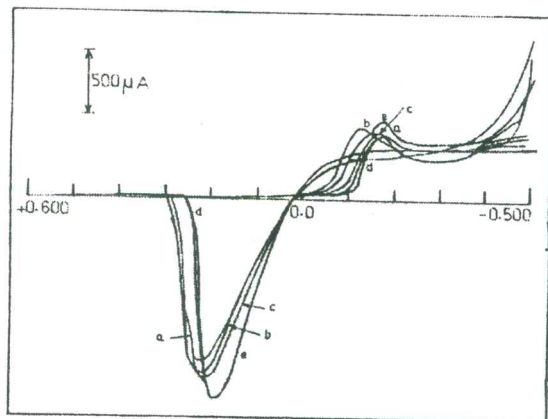


Fig. 2: Typical cyclic voltammogram in 0.04 M CuSO_4 + 0.038 M H_2SO_4 contains at different zirconium sulphate concentration
 a = 0 mM Zr (b) = 1.25×10^{-1} mM c = 2.510×10^{-1} mM
 (d) 3.75×10^{-1} mM (e) = 5×10^{-1} mM
 $E_{\lambda a} = +600$ mV $E_{\lambda c} = -500$ mV

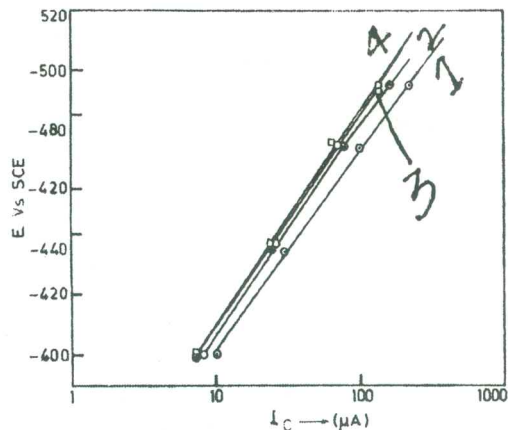


Fig. 4: E-log I_c curve for hydrogen evolution reaction
 (1) 0 mM Zr (2) 1.25×10^{-1} mM Zr
 (3) 2.5×10^{-1} mM Zr (4) 3.75×10^{-1} mM Zr

(Fig. 3). This suggests that Zr^{++} ions did not affect the reduction of copper. The mechanism of hydrogen evolution reaction was not affected as evidenced by the cathodic Tafel slope of 66 mV/decade both in presence and absence of zirconium sulphate. However the rates of hydrogen evolution reaction was hindered by zirconium sulphate and decreased appreciably with zirconium sulphate concentration.

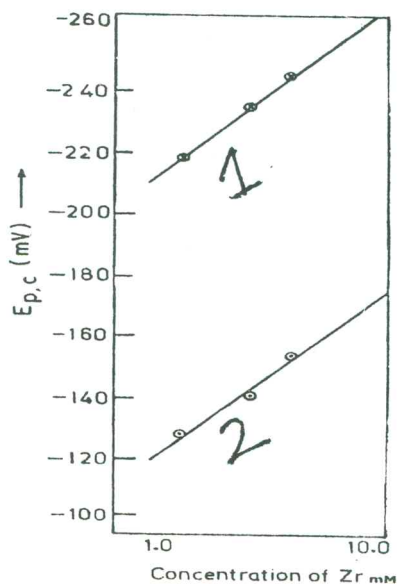


Fig. 3: Variation of cathodic peak potential with zirconium sulphate concentration at different sweep rate
 (1) 10 mV/sec (2) 25 mV/sec

CONCLUSION

Voltammetric studies carried out on platinum in acidified copper sulphate solutions revealed that the deposition of copper involves stepwise reduction of copper and the formation of monovalent copper ions is slow. The additions of zirconium sulphate in traces affected the dissolution of copper. The rates of hydrogen evolution reaction decreased with zirconium sulphate concentration.

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