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UNUSUAL CURRENT-POTENTIAL RELATIONSHIP AND MORPHOLOGY OF ELECTRODEPOSITS ON METALLIC GLASSES

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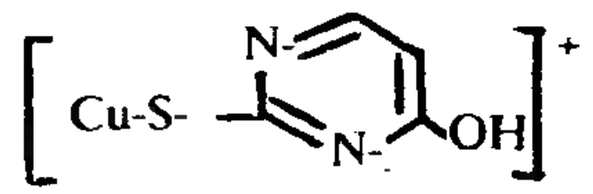
AN unusual electrokinetic and morphological observation was made on Cu-Zr metallic glasses. 2-Mercaptoethanol (MTEG) and 2-thiouracil (TUL) were used as additives in the acid copper sulphate bath. Remarkable changes in the electrokinetic parameters followed by growth habit modification were observed in the case of MTEG and TUL. Such studies are important in understanding the basic growth mechanism of the metallic glass-solution interface.

The surface of Cu-Zr metallic glass of compositions Cu_{60}-Zr_{40} and Cu_{75}-Zr_{25} was electropolished[1]. Electrode-positions were carried out at 2, 5, 10, 15, 20 and 30 mA cm^{-2} to a thickness of 3.6 μ from a highly purified[2] bath (0.25 M $CuSO_4$ + 0.1 M H_2SO_4) with a known concentration of the addition agent when ever desired. The overpotentials (η) were measured with respect to a freshly prepared copper reference electrode. The other experimental details have been described elsewhere[3]. Scanning electron micrographs of the electrodeposits were taken and examined.

The $\eta - \log i$ relationship was linear in pure solution with a slope of 116.4 mV with Cu_{60}-Zr_{40} and 136.4 mV with Cu_{75}-Zr_{25} metallic glass and the exchange current density values being 2.0 and 1.7 mA cm^{-2}. Interestingly, the presence of MTEG and TUL in the electrolytic bath lowers the Tafel slope and the exchange current density.

In the case of MTEG, from 10^{-10} mol dm^{-3} to 10^{-4} mol dm^{-3}, the Tafel slopes observed were 99.18, 98.0, 94.48, 86.08, 70.0, 58.1 and 50.0 mV. The exchange current density at the above concentrations was 1.3, 1.6, 0.8, 0.7, 0.5, 0.4 and 0.4 mA cm^{-2}. With TUL, from 10^{-6} mol dm^{-3} to 10^{-3} mol dm^{-3}, the observed values of the Tafel slope were 132.9, 101.4, 96.3 and 43.8 mV. The exchange current density at these concentrations was 2.2, 4.6, 1.5 and 1.4 mA cm^{-2}.

This unusual current-potential relationship is attributed to the formation of $[Cu\text{-}S\text{-}CH_2\text{-}CH_2\text{-}OH]^+$ electron donor-acceptor complex. This is confirmed by the IR spectral data of the scraped electrodeposit which reveals the disappearance of the absorption peak at 2550 cm^{-1} involving the –SH group in the presence of MTEG. Similarly, in the case of TUL, the changes in the electrokinetic parameters are due to the formation of



electron donor-acceptor complex confirmed by the IR spectra.

Further, the complex formed in the case of MTEG and TUL may degrade to give Cu^+ ions facilitating a rapid metal ion transfer leading to a single electron transfer, instead of a two-electron transfer, in steps, as suggested by Conway and Bockris[4] in pure solution.

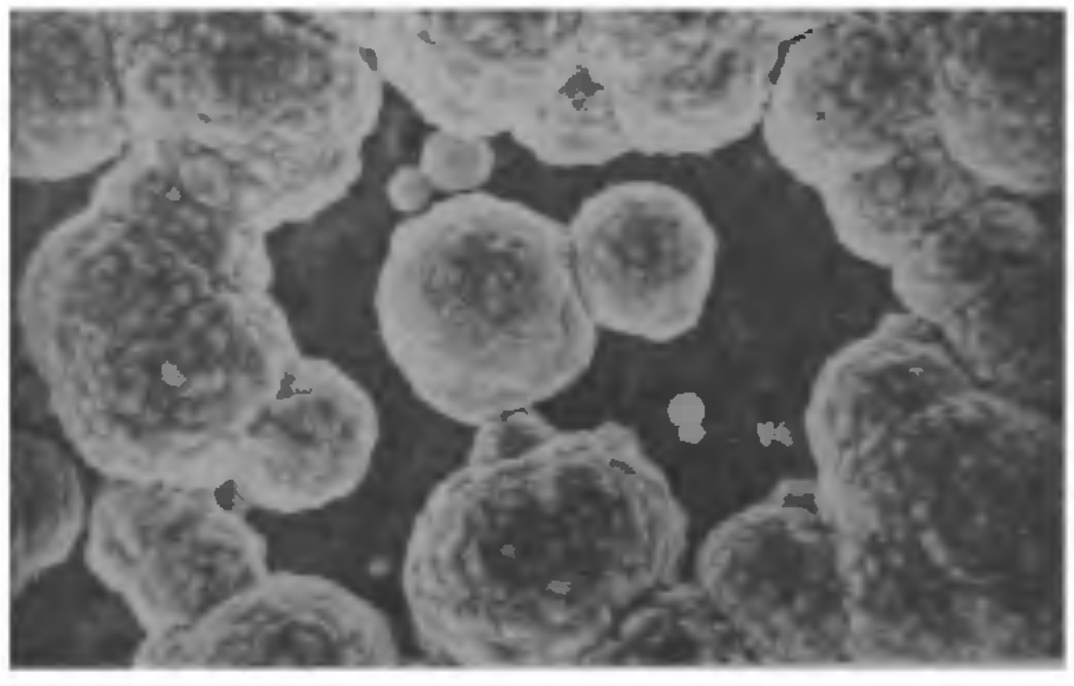


Figure 1. Scanning electron micrograph showing cluster deposit from pure acid copper sulphate bath on Cu_{60}-Zr_{40} metallic glass at 10 mA cm^{-2}.

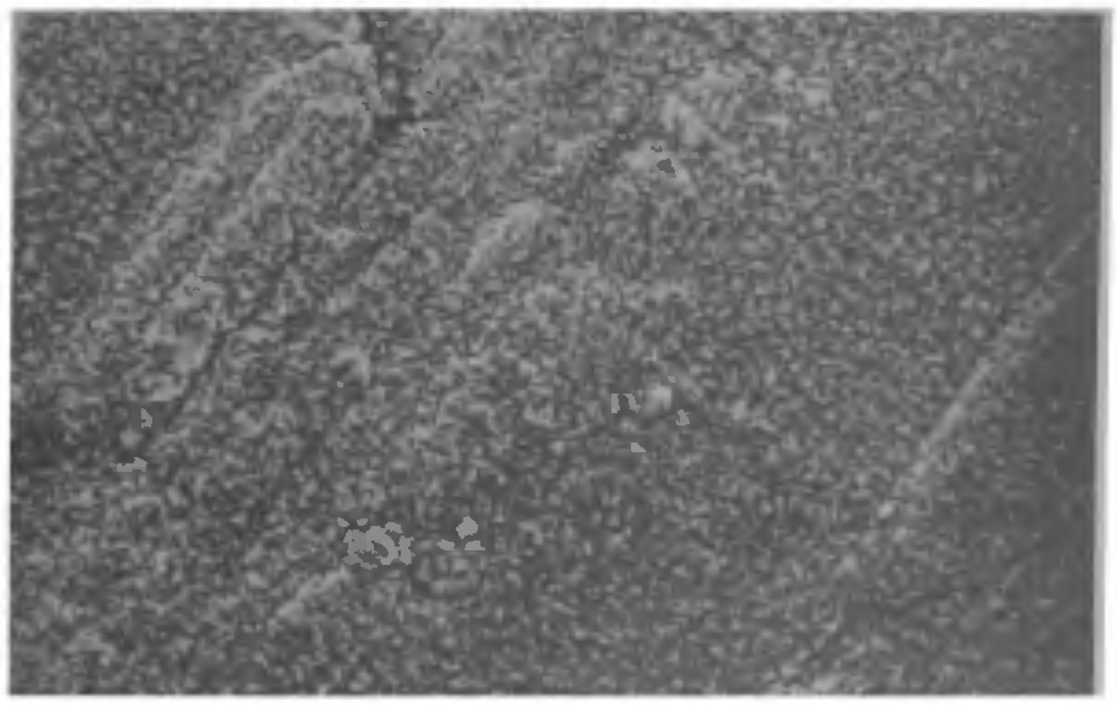


Figure 2. Scanning electron micrograph revealing a bright uniform polycrystalline deposit on Cu_{60}-Zr_{40} metallic glass with 10^{-4} mol dm^{-3} of MTEG at 10 mA cm^{-2}.

Furthermore, the changes in the electrokinetic parameters in the presence of MTEG and TUL is accompanied by a remarkable growth habit modification from cluster type of growth (figure 1) to a bright uniform polycrystalline deposit (figure 2) at the current densities studied.

The transport mechanism in the presence of MTEG and TUL is under detailed investigation.

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A NEW TRITERPENIC ESTER, FROM THE STEM BARK OF *SAPIUM EUGNIFOLIUM*

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PREVIOUS study on the *Sapium eugnifolium* has disclosed the presence of taraxerone, moretenone, taraxerol and β-sitosterol[1,2]. Our further investigation led to the isolation and structure elucidation of a new triterpenic ester (1) as well as the isolation of known compounds moretenone and β-sitosterol from the stem bark of *Sapium eugnifolium*. The structure of the new compound was established as 16,22-dihydroxy-methyl hopanoate on the basis of chemical and spectral data which is described in this note.

Compound (1) on repeated crystallization from C_6H_6-$CHCl_3$ furnished a colourless crystalline substance, m.p. 298–99°, $C_{31}H_{52}O_4$(M^+488). It responded positively to the reactions characteristic for triterpenoid but negative property to TNM. The principal peaks in the IR spectrum of (1) indicated the presence of hydroxyl (3400 cm^{-1}) and ester carbonyl (1725 cm^{-1}). The ^{1}H NMR spectrum of (1) displayed signals for the presence of seven tertiary methyl (δ0.68–1.60), an ester group (δ3.85), a broad signals for two hydroxyls (δ3.60) and a multiplet (δ4.10) due to proton attached to a carbon bearing a hydroxyl group, suggesting that one of eight methyls of a pentacyclic triterpene skeleton in (1) might be in an ester form. Acetylation (Ac_2O–C_5H_5N) of (1) at reflux temperature yielded (2), m.p. 120–22°, the IR of which showed the ester carbonyl (1725 cm^{-1}) and acetate grouping (1735 cm^{-1}). The ^{1}H NMR of (2) exhibited the presence of two acetates (δ2.00 and 2.10), and a multiplet shifted from δ4.10 (as observed in 1) to δ5.10 (in 2) in the downfield region. The above results ascribed the presence of a secondary hydroxyl and a tertiary hydroxyl in (1). The tertiary nature of one of the hydroxyl group was also confirmed by the following observations. Compound (1) on acetylation (Ac_2O–C_5H_5N) at room temperature afforded (3), m.p. 114–16°, the IR of which still showed the presence of hydroxyl (3500 cm^{-1}), ester (1725 cm^{-1}) and acetate (1740 cm^{-1}). The ^{1}H NMR spectrum of (3) indicated the presence of seven methyl (δ0.80–1.60), an ester group (δ3.85), one acetate (δ2.00) and one proton multiplet centred at δ5.10 ascribed to α-H in secondary acetate group.

These experiments were suggestive for the synthetic leucotylic acid ester (lit. m.p. 298–301°)[3]. The structure of (1) was confirmed by the following conversions to compounds of known structures. The demethylation of the compound (1) with HI yielded leucotylic acid (4), m.p. 258–60° (lit. m.p. 260°)[3]. The compound (1) on treatment with EtOH–HCl afforded methyl leucotzlidionate, (5) identified by