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Electrodeposition of copper on Cu-Zr metallic glass substrates

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This paper describes an investigation of the electrodeposition of copper on Cu-Zr metallic glass in the presence of 5-sulphosalicylic acid and 2-thiouracil. The observed morphological features and electrokinetic parameters are correlated, and suitable transport mechanisms are proposed with the help of infrared studies. It was observed that Cu-Zr metallic glasses enhance the rate of decomposition of hydrogen peroxide catalytically and electrocatalytically. This was attributed to the unusual structure of the substrate and physical or chemical inhomogeneities.

1. Introduction

A large number of studies on the structure and properties of metallic glasses have been reported in the literature, including a few on their corrosion, electrochemical, catalytic and electrocatalytic properties [1–6]. Metallic glasses possess distinctive chemical composition, unique geometric or topological order, freedom from constraint of periodicity and requirements of stoichiometry.

An investigation on the behaviour of the glassy state during the deposition of copper from pure solution and the functional group effect in the overall performance of the addition agent with varying current density is a novel one, in addition to the known catalytic and electrocatalytic properties of metallic glasses. Such studies may aid our understanding of the chemical and electrochemical behaviour of metallic glasses and explain some of their unusual properties.

In the present work, the electrodeposition of copper from highly purified solutions of copper sulphate was carried out on Cu-Zr metallic glass in the absence and presence of 5-sulphosalicylic acid and 2-thiouracil, to examine the substrate effect, the role of $-SO_3H$, $-COOH$, and $-SH$ groups present in the additives and the effect of current density etc. Further, Cu-Zr metallic glasses were used for the catalytic and electrocatalytic decomposition of hydrogen peroxide. The observed behaviour was related to the structure.

2. Experimental details

Cu-Zr metallic glasses, supplied by the University of Leeds, England, were used as substrates for electrodeposition and catalytic and electrocatalytic studies.

Cu_{75}-Zr_{25} metallic glass of one square cm surface area was used as cathode for the electrodeposition of copper. The cathode was mechanically polished and electropolished [7] in a phosphoric acid bath. A highly purified bath of $0.25\,mol\,dm^{-3}$ of $CuSO_4$ and $0.1\,mol\,dm^{-3}$ of H_2SO_4 was used to carry out the electrodeposition of copper at various current densities of 2, 5, 10, 20, and $30\,mA\,cm^{-2}$ to a deposit thickness corresponding to $10\,C\,cm^{-2}$ (3.6 microns) in the absence and presence of various concentrations of 5-sulphosalicylic acid (SSA) and 2-thiouracil (TUL). Overpotentials (η) during deposition were measured using an Elico Model digital millivoltmeter with respect to a freshly prepared copper reference electrode and the accuracy compared with a freshly prepared Hg/Hg_2SO_4 electrode for reproducibility. The other experimental details have been described elsewhere [8].

0.15 g of Cu_{55}-Zr_{45} metallic glass was weighed and used for the catalytic decomposition of hydrogen peroxide, and two square centimeter surface area of Cu_{55}-Zr_{45} and $Cu_{27.5}$-$Zr_{72.5}$ metallic glasses were used for the anodic electrocatalytic decomposition of hydrogen peroxide at $0.25\,mA\,cm^{-2}$, following standard procedures.

3. Results

3.1. *Morphology*

3.1.1. At $2\,mA\,cm^{-2}$. When copper was deposited on Cu_{75}-Zr_{25} metallic glass, a cluster type of deposit was observed in pure solution. The cluster type of growth changed to irregular blocks when the concentration of SSA was $10^{-9}\,mol\,dm^{-3}$, followed by a decrease in the size with an increase in the concentration to $10^{-4}\,mol\,dm^{-3}$. On further increasing the concentration of SSA to $10^{-2}\,mol\,dm^{-2}$, the small irregular blocks spread to give rise to a polycrystalline deposit.

In the presence of TUL, the clustered deposit observed in pure solution changed to a uniform polycrystalline deposit at $10^{-6}\,mol\,dm^{-3}$, with a decrease in the grain size up to $10^{-3}\,mol\,dm^{-3}$ of the additive in the electrolytic bath.

3.1.2. At 5 and $10\,mA\,cm^{-2}$. A clustered and non-uniform polycrystalline deposit was observed in pure solution (Fig. 1c). Big granular deposits were obtained with 10^{-9} and $10^{-7}\,mol\,dm^{-3}$ of SSA. Grain refine-

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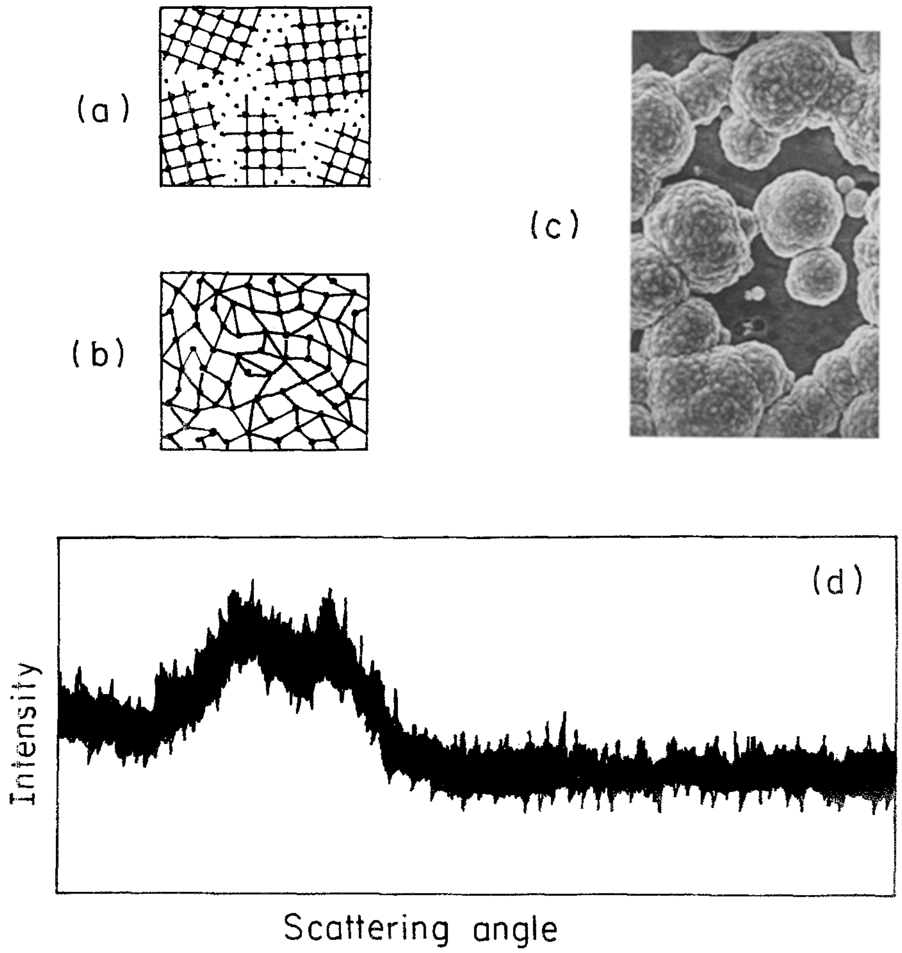


Fig. 1. Schematic diagram of models proposed for the disordered structure, scanning electron micrograph showing cluster deposit and X-ray diffractogram of Cu-Zr metallic glass. (a) Microcrystalline disorder model; (b) Topological disorder model; (c) SEM showing cluster type of deposit from pure acid copper sulphate bath on Cu_{75}-Zr_{25} metallic glass at $10\,mA\,cm^{-2}$; (d) X-ray diffractogram of Cu-Zr metallic glass.

ment occurred at $10^{-4}\,mol\,dm^{-3}$ of SSA (Fig. 2), with dark triangular blocks appearing here and there at $10^{-2}\,mol\,dm^{-3}$.

With TUL, a polycrystalline deposit with big grains was noticed with $10^{-6}\,mol\,dm^{-3}$ in the bath. A fine grained polycrystalline deposit was obtained at $10^{-5}\,mol\,dm^{-3}$ (Fig. 3c) which turned dull on increasing the concentration of TUL to $10^{-3}\,mol\,dm^{-3}$.

3.1.3. At 20 and 30 mA cm^{-2}. A polycrystalline deposit observed in pure solution revealed grain refinement with low and moderate concentrations of SSA and turned dull at high concentration ($10^{-2}\,mol\,dm^{-3}$), at $20\,mA\,cm^{-2}$. However, at $30\,mA\,cm^{-2}$, the polycrystalline deposit turned dull at all concentrations studied.

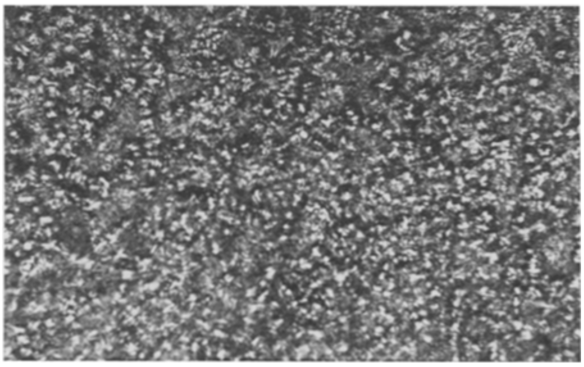


Fig. 2. Polycrystalline deposit of copper on Cu_{75}-Zr_{25} metallic glass from acid copper sulphate bath in the presence of $10^{-4}\,mol\,dm^{-3}$ of SSA at $10\,mA\,cm^{-2}$ (625 ×).

In the presence of TUL, a polycrystalline deposit with big grains was noticed at $10^{-6}\,mol\,dm^{-3}$. Refined grains were observed at $10^{-5}\,mol\,dm^{-3}$ which turned dull at $10^{-3}\,mol\,dm^{-3}$. At $30\,mA\,cm^{-2}$, a dull deposit was observed at all concentrations of TUL.

3.2. *Overpotentials*

The reproducibility of the overpotential curve varies with the current density. Hence, it is only possible to give a qualitative evaluation of the results obtained. The values fluctuate at the initial stages of deposition. Hence, evaluation of electrokinetic parameters are based on the final η values obtained at a thickness corresponding to $10\,C\,cm^{-2}$. The overpotential values decreased with time at the current densities studied and reached a constant value. A plot of the final overpotential values against the concentration of SSA and TUL at various current densities revealed a minimum at $10^{-7}\,mol\,dm^{-3}$ in the case of SSA and a sudden decrease of $10^{-3}\,mol\,dm^{-3}$ of TUL (Fig. 4).

The current potential curves obtained for the electrodeposition of copper from pure solutions and in the presence of various concentrations of SSA and TUL on Cu_{75}-Zr_{25} metallic glass revealed changes in the Tafel slope (b) and exchange current density (i_0) values, shown in Table 1.

3.3. *Infrared spectral data*

In the spectrum of 5-sulphosalicylic acid, there are

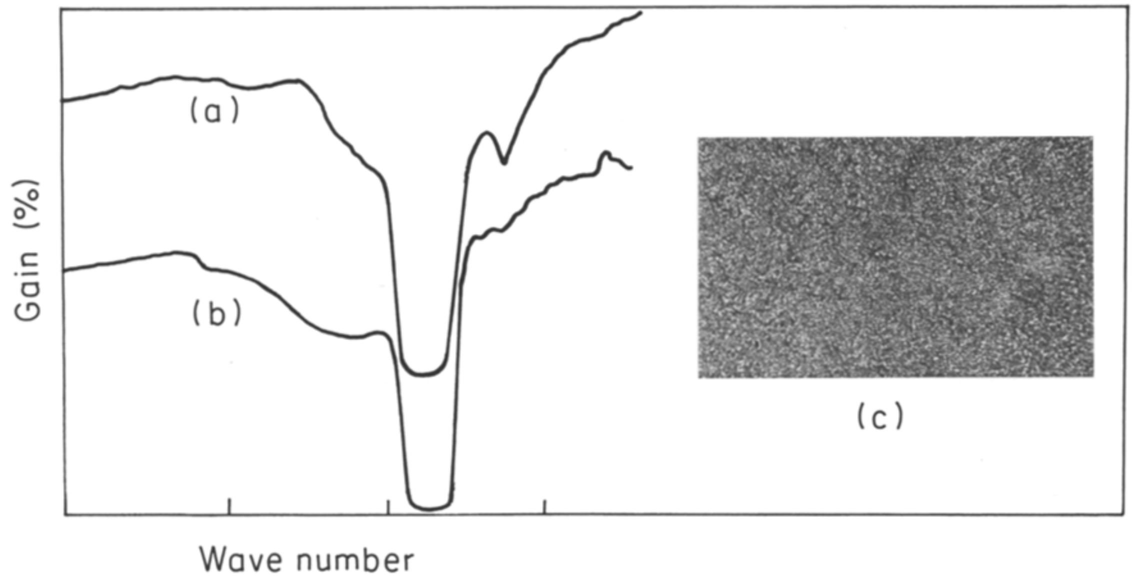


Fig. 3. Infrared spectra of (a) 2-thiouracil; (b) copper-thiouracil complex; (c) fine grained polycrystalline deposit of copper on Cu_{75}-Zr_{25} in the presence of 10^{-5} mol dm^{-3} of 2-thiouracil at 10 mA cm^{-2} (625 ×).

absorption peaks at 1210 cm^{-1} and 1610 cm^{-1} corresponding to the stretching vibrations of the $-SO_3H$ and $-COOH$ groups, and at 2550 cm^{-1} corresponding to the stretching frequency of the –SH group for 2-thiouracil. In the spectra of the compound obtained with copper sulphate solution in the presence of TUL, the –SH peak was absent (Fig. 3a,b).

3.4. *Catalytic behaviour of Cu_{55}-Zr_{45} metallic glass*

The catalytic activity of Cu_{55}-Zr_{45} metallic glass for the decomposition of hydrogen peroxide was obtained from a plot of logarithm of the volume of potassium permanganate consumed against time, and compared with a plot obtained without the catalyst and also in the presence of crystalline copper and zirconium, at various temperatures. The calculated rate constant at various temperatures in the presence of Cu_{55}-Zr_{45} metallic glass revealed a faster rate of decomposition of hydrogen peroxide (Table 2).

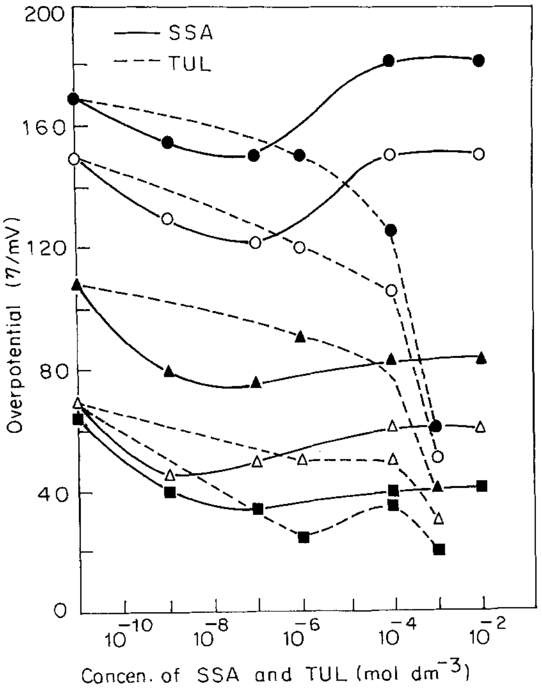


Fig. 4. Final overpotential versus concentration of SSA and TUL during the electrodeposition of copper on Cu_{75}-Zr_{25} metallic glass at 2 (■); 5 (△); 10 (▲); 20 (○) and 30 (●) mA cm^{-2}.

3.5. *Electrocatalytic behaviour of Cu_{55}-Zr_{45} and $Cu_{27.5}$-$Zr_{72.5}$ metallic glasses*

The titre values for the electrocatalytic decomposition of hydrogen peroxide in the presence of Cu_{55}-Zr_{45} and $Cu_{27.5}$-$Zr_{72.5}$ metallic glasses at room temperature in the absence and presence of H_2SO_4 and HCl at 0.25 mA cm^{-2} revealed an enhanced activity when compared to those obtained in the presence of crystalline copper and zirconium. The rate constants for the anodic reactions are given in Table 3.

4. Discussion

The overpotential values observed at the initial stages of deposition are highly chaotic and irregular due to the disordered structure supporting the microcrystalline disorder model [9]. The observed growth characteristic of a cluster type of deposit in pure solution reveals the influence of the Cu-Zr glassy substrate with a short range order and long range disorder (Fig. 1).

The changes in the Tafel slope and exchange current density values (Table 1) in the presence of SSA and TUL, as seen from the overpotential versus current density curves indicate that the additives, through their functional groups, influence the growth characteristics of copper electrodeposits from clusters to irregular deposits and then to uniform fine grained polycrystalline deposits (Fig. 3) at the critical concentration as seen from the infrared spectra, and precipitation of the additives at high concentrations leading to dull deposits.

The probable transport mechanisms with SSA and

Table 1. Electrokinetic parameters 'b' and 'i_0' for the electrodeposition of copper on Cu_{75}-Zr_{25} metallic glass in the presence of SSA and TUL

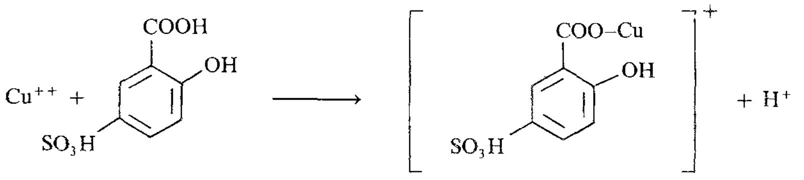
Addition agent	*Concentration* ($mol\,dm^{-3}$)	*Tafel slope* ($\pm 10\,mV$)	*Exchange current density* ($mA\,cm^{-2}$)
	Pure solution	136.4	1.7
5-sulphosalicylic acid	10^{-8}	138.2	2.4
	10^{-7}	135.9	2.0
	10^{-4}	149.5	2.0
	10^{-2}	150.3	2.0
2-thiouracil	10^{-6}	132.9	2.2
	10^{-5}	101.4	4.6
	10^{-4}	96.3	1.5
	10^{-3}	43.8	1.4

Table 2. Rate constants for the catalytic decomposition of hydrogen peroxide

Catalyst	*Rate constant (min^{-1}) by graphical method*		
	$25 \pm 1°C$	$40 \pm 1°C$	$50 \pm 1°C$
No catalyst	2.559×10^{-5}	6.579×10^{-5}	7.658×10^{-5}
Cu_{55}-Zr_{45} metallic glass	1.536×10^{-4}	3.948×10^{-4}	7.036×10^{-4}
Copper	7.675×10^{-5}	2.193×10^{-4}	3.581×10^{-4}
Zirconium	1.228×10^{-4}	2.558×10^{-4}	4.092×10^{-4}

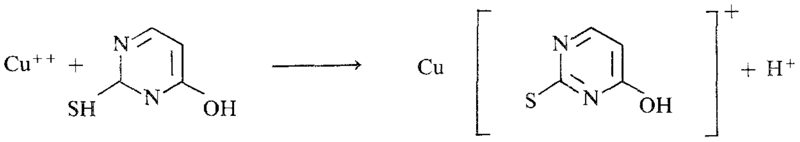
TUL are:

With SSA:



(1)

With TUL:



(2)

Thus, in the absence of SSA and TUL, a cluster type of growth occurs due to the substrate effect and fine grained polycrystalline and dull deposits in the presence of SSA and TUL due to adsorption, complexation and precipitation on the substrate.

The increase in the *k* value for the catalytic decomposition of hydrogen peroxide in the presence of Cu_{55}-Zr_{45} metallic glass may be due to lower ionization energy, lower electronegativity and higher oxidation state of zirconium [10] compared to copper in addition to the glassy structure and lattice mismatch of the substrate, thus favouring a basic site which involves in

Table 3. Rate constants for the anodic electrocatalytic decomposition of hydrogen peroxide in the absence and presence of H_2SO_4 and HCl

Catalyst	*Rate constant (min^{-1}) by graphical method at $0.25\,mA\,cm^{-2}$*
Cu_{55}-Zr_{45} metallic glass	1.364×10^{-2}
$Cu_{27.5}$-$Zr_{72.5}$ metallic glass	1.961×10^{-2}
$Cu_{27.5}$-$Zr_{72.5}$ metallic glass + 0.1 M H_2SO_4	4.094×10^{-3}
$Cu_{27.5}$-$Zr_{72.5}$ metallic glass + 0.001 M HCl	5.117×10^{-3}
Copper	7.311×10^{-4}
Copper + 0.1 M H_2SO_4	3.684×10^{-3}
Copper + 0.001 M HCl	4.913×10^{-3}
Zirconium	3.862×10^{-3}

the following reaction pathway:

$$B^- + H_2O_2 \longrightarrow B^-H^+ + HO_2^- \quad (3)$$

$$HO_2^- + H_2O_2 \longrightarrow H_2O + O_2 + OH^- \quad (4)$$

The observed increase in the anodic electrocatalytic activity in the presence of Cu-Zr metallic glasses is due to polarization leading to a more basic character of the substrate.

Thus, it may be concluded that at the initial stages of deposition, the substrate influences the morphology and electrokinetic parameters, the additives at moderate concentration bring growth habit modification and at high concentration favour random nucleation. The catalytic activity may be attributed to the basic character and the electrocatalytic activity to a more basic character of the metallic glass substrate, due to anodic polarization.

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