The effect of surfactants on the electropolishing behavior of copper in orthophosphoric acid

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ABSTRACT

The electropolishing behavior of copper was studied in orthophosphoric acid with Triton X-100, sodium dodecyl sulphate and cetyl pyridinium chloride as additives for improving the finish obtained on copper surface. This was investigated by measuring and comparing anode potential-limiting current relationships in solutions of gradually increasing concentration of surfactants. The addition of surfactants to the electropolishing solution results in a lower limiting current. This confirms the mass transport of dissolved species from the anode surface to the bulk of solution as the rate-determining step in the presence of three surfactants in all concentrations investigated. Scanning electron microscope (SEM), atomic force microscope (AFM) and measured brightness values were used to investigate the copper surface after electropolishing and the results were compared to polishing done in absence of surfactants. According to SEM images and brightness values, addition of Triton X-100 was effective to enhance levelling and brightening more than sodium dodecyl sulphate and cetyl pyridinium chloride. AFM analysis showed that the roughness values (R_a) for an electropolished copper surface, in presence of surfactants, is significantly lower than in absence of surfactants. Different reaction conditions and the physical properties of solutions are studied to obtain dimensionless correlation among all these parameters.

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1. Introduction

The electropolishing (EP) has been used for various purposes in research and industry for many years. The appropriate formulation of the electropolishing solutions, EP conditions and the process application itself were and are still the subject of numerous trade secrets and patents [1,2].

The practical aspects of EP have been reviewed by Mohan et al. [3], whereas the most fundamental aspects are covered in a review by Landolt [4]. The surface phenomena of EP are generally classified into two processes: anodic levelling and anodic brightening. Anodic levelling results from a difference in the dissolution rate between peaks and valleys on a rough metal/alloy surface depending on the current distribution or mass-transport conditions [5]. It is usually associated with a decrease of roughness in the micrometer or large range [4]. Anodic brightening, on the other hand, can be achieved only under the conditions in which the metal dissolution is mass-transport-controlled and the formation of a precipitated salt layer at the electrode surface is possible. The presence of salt layer can suppress the influence of crystallographic orientation and surface defects on the dissolution process. This phenomenon will lead to

microfinishing in the submicrometer scale and specular reflectivity of metals/alloys can be obtained [6–9].

Copper surface seems rough and complex under microscopic investigation, due to the presence of macro and micro scales of humps and depressions. It has received much attention due to its practical and academic interests, some workers tried to attain bright and smooth surface of copper, aluminium, stainless steel and other alloys by applying EP methods [10–12]. Edson [13] studied the brightening of copper, silver and gold by using an electrolytic solution composed mainly of thiourea and some additives such as polysaccharides as reducing materials and mineral acids as conductivity improvers.

Others studied EP of copper using additives such as soluble starch, ethylene glycol and methanol to achieve smooth and highly lustrous copper surface [14]. Furthermore addition of ethylene glycol and glycerol [15], tert-butanol [16], amines [17], amino acids [18] and aldehydes [19] improved planarization efficiency of copper surface, where the up and down thickness differences are eliminated.

In this study, an attempt is extended to reduce the roughness of the surface by reducing the etched pits and defects formed over the surface, consequently, the surface smoothness and brightness could be increased. Accordingly, the present work is aimed to study the effect of addition of surface active agents (SAS) to orthophosphoric acid solutions used as electrolytes for EP of copper.

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Table 1
Chemical composition of copper.

Element	Cu	Cd	Ag	P	Ni	Fe	Zn	Pb	Sn
wt%	99.98	0.001	0.001	Negative	Negative	Negative	Negative	0.003	0.005

The SAS chosen for examination were nonionic surfactant namely Triton X-100, anionic surfactant namely sodium dodecyl sulphate (SDS) and cationic surfactant namely cetyl pyridinium chloride (CPC) which were available in purified form. The SAS chosen offer variation in the chain length of the hydrocarbon portion, and the type of the polar portion. SAS have many advantages such as high inhibition through adsorption on the metal surface, low price, low toxicity and easy production.

It is well known that SAS are characterized by critical micelle concentration (so called CMCs). The CMC is the concentration, where SAS in solution change their initial molecular solvated state. Most of the physical and chemical properties of SAS solutions undergo an abrupt variation at this concentration. This effect is

of luggin tube filled with orthophosphoric acid–organic solution similar to that in the cell. The tip of the luggin tube was placed 0.5–1 mm from anode wall. Polarization curves, from which the limiting current was determined, were plotted by increasing the applied current stepwise and measuring the corresponding steady-state potential. Two minutes were allowed for reaching the steady state potential. Before each run, the back of anode was insulated with polystyrene lacquer and the active surface was polished with fine emery paper, degreased with trichloroethylene, washed with alcohol and finally rinsed in distilled water with a measured resistivity >18 MΩ/cm. The temperature was regulated by placing the cell in thermostatic water bath at $25 \pm 0.5\,°C$. The copper sheets used in the present work have the composition shown in Table 1.

The structure of SAS is given below:

Triton x-100 (n = 10)

Sodium dodecyl sulphate (SDS)

Cetyl pyridiunium chloride (CPC)
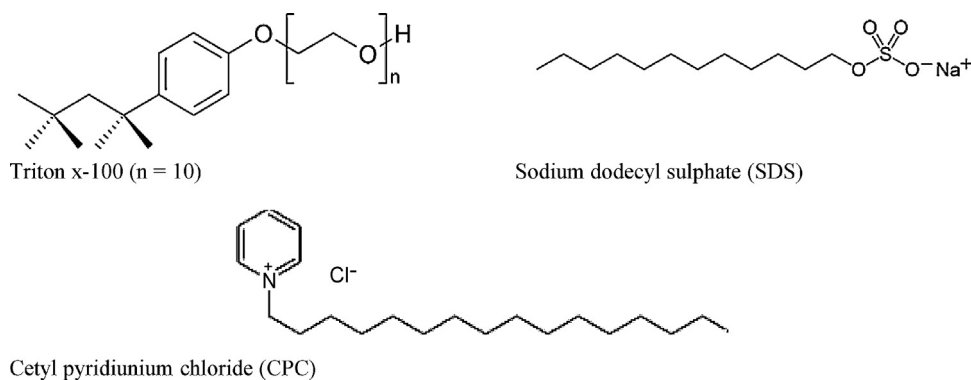
of interest for theoretical reasons as well as for practical application.

In the present study, potentiodynamic polarization measurements were performed to examine the EP process of pure copper in H_3PO_4 acid in the presence of these SAS, for the range of concentrations below, at and above CMC. The extent of polishing was assessed through an elaborate study relating the influence of SAS concentrations (and type) and the resulting surface morphology (investigated by SEM), surface topography (investigated by AFM) and surface brightness. Physical properties of the solutions such as density, viscosity and diffusion coefficient were studied to obtain a dimensionless correlation among all parameters.

2. Materials and methods

2.1. Potentiodynamic measurements

The cell used in the present work consists of rectangular container having the dimensions of $5\,cm \times 10\,cm$ with electrodes fitting the whole cross section. The electrodes were rectangular copper sheets of 10 cm height and 5 cm width. Cathode–anode distance was 5 cm. The electrical circuit consisted of a 6 V D.C. power supply, a variable resistance and a multi range ammeter connected in a series with cell. A high impedance voltammeter was connected in parallel with the cell to measure its potential. Five concentrations of orthophosphoric acid (6, 8, 10, 12 and 14 M) were prepared from analar grade H_3PO_4 (85%). Ten concentrations of surfactant solutions (Triton X-100, sodium dodecyl sulphate and cetyl pyridinium chloride) with 8 M H_3PO_4 are used ranging from 5×10^{-7} M to 1×10^{-2} M. The steady state anode potential was measured against reference electrode consisted of copper wire immersed in a cup

2.2. Surface tension measurements

The surface tension was measured at 25 °C using Du Nouy tensiometer (Kruss type 8451) for various concentrations of the surfactants additives. The temperature ($\pm 0.1\,°C$) was kept constant by circulating the thermostatted water through a jacketed vessel containing the solution.

2.3. Density and viscosity measurements

The density (ρ) and viscosity (μ) of different solutions were used to calculate the dimensionless groups Sherwood (Sh), Schmidt (Sc) and Grashof number (Gr) (Table 2). The density was measured by using DA-300 Kyoto electronic instrument. The viscosity was measured by using Koehler viscosity bath (model K23400). The accuracy of the instrument is 2%.

2.4. Diffusion coefficients measurements

The diffusion coefficient of blank solution and of solutions in the presence of different concentrations of SAS used in this study were calculated by measuring the limiting current of the anodic dissolution of a copper rotating disc in H_3PO_4 and applying the Levich equation [15]:

$$i_L = 0.62nFD_{eff}^{2/3}\gamma^{-1/6}(C_{sat,Cu} - C_{b,Cu})\Omega^{1/2} \qquad (1)$$

where $i_L = I_L/A$. i_L is the limiting current density (A cm^{-2}), A is the cross-sectional area of Cu disc, n is the number of electrons involved in the reaction, F is Faraday constant, D_{eff} is the effective diffusion coefficient of dissolving species, γ is the kinematic viscosity, Ω is