Abstract

Electrodeposition/electroplating is a versatile technology employed in multiple industries because of its precise control over material deposition, and capacity to improve or alter surface properties. A wide range of materials can be electrodeposited, and the choice of material depends on the desired properties of the final product, like appearance, corrosion resistance, conductivity, hardness, etc. Electrodeposition of precious metals like gold (Au), silver (Ag) and their alloys with other metals are used extensively across many industries owing to their unique properties such as high electrical conductivity, resistance against tarnishing, aesthetic appeal, etc. The industrial process of gold and silver electrodeposition involves the use of toxic cyanide-based baths, which are considered as a significant environmental threat. This has resulted in efforts to formulate cyanide-free electroplating baths for the deposition of gold and silver. In the quest for the development of cyanide-free electroplating baths for gold and silver, researchers across the globe have identified and tested a few complexing agents and additives that can be used to stabilize the metal ions in the plating solution. However, it observed that there is plenty of room for further research in this domain. Therefore, the primary objective of this thesis is to develop a novel cyanide-free electroplating bath for the deposition of silver and gold, while investigating how the electrodeposition process, plating parameters, and surfactant polarity impact the structural properties, surface morphology, mechanical attributes, and resistance to tarnishing. Additionally, the deposition of Ag and Au with copper is carried out to study the effect of current density on various coating properties.

A novel cyanide-free bath containing sodium thiosulphate as the main complexing agent is developed for the deposition of Ag coatings. A comparative assessment of electrodeposition routes, i.e., direct current (DC) and pulse galvanostatic (PG) electrodeposition, is carried out to study the effect of plating route and current density on the coating properties. Highly compact and adherent Ag coatings with a mirror-finish appearance are obtained via pulse

galvanostatic route. After optimizing the deposition route, the study investigates the effect of cationic surfactant (CTAB) on the electrochemical, structural, and anti-tarnishing properties of Ag coatings. Subsequently, the electrodeposition of bimetallic Cu-Ag coatings is investigated from a thiourea (TU)-based bath, and the effect of current density on surface morphology, mechanical properties and the electrical resistivity is studied. The electrical resistivity of the developed Cu-Ag bimetallic coatings is similar to that of bulk Ag, suggesting that it can be a good replacement for electrical contact materials.

Mirror-bright Au coatings are deposited from a thiosulphate-based bath via pulse galvanostatic route at different current densities. With an increase in the current density, there is an increase in the coating thickness, concentration of Au, and surface roughness of the coatings. The coatings deposited at 10, 50, 100 and 200 mA/cm2, have a hardness of ~294, 271, 211, and 190 VHN, respectively. Nano scratch test is employed to verify the adherence of the coatings. The influence of CTAB on the morphology and the anti-tarnishing performance of the Au coatings is also investigated. Experimental as well as theoretical studies show that the severity of tarnishing is lower for coatings electrodeposited from the bath containing CTAB. Additionally, the prospects for the deposition of Au from non-aqueous bath is also explored using a choline chloride-ethylene glycol (ChCl-EG) based bath, and the effect of current density and surfactant polarity on the type of nucleation and growth occurring, morphology of the coatings and their anti-tarnishing performance is investigated. In the presence of cationic surfactant, the coating has a smooth and compact surface with a globular morphology. In presence of anionic surfactant, the coating morphology changes from globular to sharp-edged facets, and with non-ionic surfactant there is an irregular faceted morphology. The coating deposited from the bath containing cationic surfactant offers better resistance against tarnishing.

Gold-copper (Au-Cu) alloy coatings are successfully deposited from a thiourea (TU)-based bath, and the effect of current density on the morphology, mechanical properties, and anti-

tarnishing performance of the coatings is investigated. The SEM investigations show a wide variation in the surface morphology of the coatings, from clustered agglomerates to fine grain, as the current density increases. Additionally, it is observed that there is an increase in the coating thickness, hardness, adhesive strength, and resistance against tarnishing upon increasing the applied current density.

Keywords: *Cyanide-free; gold electroplating; silver electroplating; surfactants; electrodeposition; pulse galvanostatic.*