Ph.D.Thesis of Salahaddin University-Erbil Academic Staff Studied Abroad

Title of thesis:ELECTRODEPOSITION OF CHROMIUM USING NOVEL DEEP EUTECTIC SOLVENTS

Name: Azeez Abdullah Azeez **Supervisors:**Prof Andrew P. Abbott&Prof Karl S. Ryder
Department/College: Physics/ Education **Department/College:** Materials Science Centre / Science
Email: azeez.azeez@su.edu.krd **University/Country: Leicester/ UK**
Mobilee: 00964(0)750 454 2010 **Email:** aa1@le.ac.uk
Period of Study: from 03/10/2011 to 30/09/2014

Summary(Abstract):
Chromium electrodeposition is important for the production of anti-wear and anti-corrosion coatings. It has been carried out for over 50 years in a multi-billion dollars industry using essentially the same technology based on chromic acid. The toxicity of the electrolyte makes the search for an alternative process an environmental imputative.
In this study a variety of novel formulations of deep eutectic solvents are produced and tested to determine their efficacy for chromium deposition. The study concentrates on using urea as a complexing agent with a variety of trivalent chromium salts.
In the first results chapter complexes of $CrCl_3 \cdot 6H_2O$ with urea are formed. It is shown that this system displays high conductivities, despite relatively high viscosities compared with the previously reported chromium based deep eutectic solvents. Thick, adherent, non-cracked black chromium could be deposited and produce relatively hard chromium coatings. EXAFS suggests that there are a variety of chromium species but they are probably cationic with a variety of oxygen donors as ligands.
In the next section $[Cr(en)_3]^{3+}$ species was produced as the cationic species and this had a higher conductivity than any similar system previously described. Bright, adherent, hard chromium was obtained by electroreduction with constant speciation. A novel solvatochromic shift, that we are unaware of in the literature, demonstrates the charge transfer complex results in an unexpected colour change.
In an endeavour the remove of Cl^- from the formation chrome-alum ($KCr(SO_4)_2 \cdot 12H_2O$) was used as the metal salt. This produced unprecedented high conductivity for this type of medium with a low viscosity. It was proposed that unlike most ionic liquids mass transport is not limited by hole transport and instead it is proposed that these liquids function more like very concentrated electrolytes where ion paring becomes important.
In the final result section a variety of additives are tested. Some are shown to have a significant effect on the morphology and hardness of the deposit. Ultimately bright metallic chromium films could be reproducibly produced with a hardness of 800±10 HV. This is the first process based on Cr(III) to be able to achieve these rigorous requirements and suggests the first real alternative to hexavalent chromium for hard chrome.
Acknowledgment: I would like to record my great appreciation for Salahaddin University-Erbil-Kurdistan (http://international.su.edu.krd), for giving me the permission leave and giving me full salary study permission for the whole period of the study abroad.