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The Study of the Effect of Surfactants on Copper Codeposition with SiC Nano Particulate from Deep Eutectic Solvent Ionic Liquids (Ethaline)

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Authors' contributions

This work was carried out in collaboration between both authors. Both authors read and approved the final manuscript.

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ABSTRACT

Here we investigate the electrolytic deposition of copper and copper nano composites in the absence and the presence of two types of surfactants: cationic which is sodium dodecyl sulphate (SDS) and the other type is cetyl trimethyl ammonium bromide (CTAB) from a solution of the metal chloride salt in ethylene glycol–choline chloride based eutectics. The SEM images and EDAX analysis allow in situ quantification or particulate inclusion. It is quite interesting to perceive that the composition of composite material was strongly dependent on the amount of species suspended in solution. Again the data here has revealed that the majority of material was dragged onto the surface rather than settling on to it. The distribution of the composite material was found to be even throughout the coating. This technology is important because it facilitates deposition of bright copper coatings without co-ligands such as cyanide which is not friendly environment.

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1. INTRODUCTION

"One of the prospects to increase the stability and execution of materials for different utilizations is to fortify them using composite coatings. In contemporary years, there has been a rise in interest in the development of wear-resistant coatings" [1]. Commercially, the surface of a mass material is plated with a material having a high degree of wear resistance.

"Such coatings can be economically realized by co-depositing various fine and inert particles into a metallic matrix from an electrolytic bath" [2-8]. "Co-sedimentation of particles in a metal matrix is the consequence of the adsorption of metal ions at the particle surface and thus let them attracted to the negative pole" [9]. "The role of the particles presence in the electrolyte on mass transfer enhancement and the influence of hydrodynamic circumstances on the particle content in codeposits has also been explored" [10,11]. The rate of the deposition and mechanism of inert particles from electrolytic baths has been investigated by Guglielmi [12] and Celis and Roos [13]. Celis et al [14] proposed a mathematical model for electrolytic co-deposition of particles with a metallic matrix. Stankovic and Gojo [15] electrodeposited composite coatings of copper with inert, semi-conductive and conductive particles. The involvement of second phase particles in the electrolytic deposition of metals enhances the mechanical properties, corrosion resistance, surface texture, etc.

"The electrodeposition of metals, metal alloys and composites (second phase dispersed material) using ionic liquids has been investigated and applied on electroplating industries extensively. The advantages of these novel solvents include: electroplating electronegative metals, e.g. Al, Ta, Nb, Mo, W; direct electroplating of metals on water sensitive substrate materials such as Al and Mg can be achieved, removal of hydrogen embrittlement from the substrate; alloy deposition is easier to achieve; the possibility exists to develop novel immersion plating baths; potential energy savings compared with aqueous solutions; replacement of many hazardous and toxic materials currently used in water, e.g. Cr(VI), cyanide; and access to novel deposit morphologies" [16-21].

"In previous studies we examined the composites of copper with Al_2O_3 and SiC have also been produced and we show that the proportion of these species incorporated into the resulting electroplated films is determined by the mass loading in the solution. The main mechanism for particulate inclusion is drag onto the electrode surface. The inclusion of suspended particles in the liquid is found to have negligible effect upon the fluid viscosity of the suspension; we propose that this is a consequence of the increased free volume in the fluid component caused by the motion of the suspended particles, i.e. the particles act as micro stirrers in the liquid [22].

"The electrodeposition of copper is vital and required for tremendous application in any field of society like a variety of industrial and decorative purposes including large scale use in the electronics industry for production of printed circuit boards, selective case hardening of steel for engineering components, and production of electrotypes in the printing industry [23,24]. "Copper may be easily deposited and electroplated with other metals and it is therefore particularly useful as a pre-coating for soft soldered work or for zinc alloy die-castings used by the automotive industry. In these cases the copper deposit provides a protective layer to the metal to allow further coatings to be applied" [25]. "Also the incorporation of particulate material into metal coatings has become an area of technological interest; for example incorporation of poly(ethylene) can act as a corrosion barrier, incorporation of PTFE or mica can reduce surface friction whereas incorporation of alumina, silicon carbide, boron nitride or diamond can greatly increase hardness of the metal coating" [26].

2. EXPERIMENTAL DETAILS

2.1 Preparation of IL

Choline chloride [$HOC_2H_4N(CH_3)_3Cl$] (ChCl) (Aldrich 99%) was recrystallised from absolute ethanol, filtered and dried under vacuum. Urea (Aldrich .99%) was dried under vacuum before use. Ethylene glycol (EG) (Aldrich 99z%), copper chloride dihydrate, were all used as received. The eutectic mixtures were formed by stirring the two components together, in the stated proportions, at 75^{o}C until a homogeneous, colourless liquid formed. 0.1 M $CuCl_2$. $2H_2O$ each dissolved in1 Choline Chloride : 2 ethylene glycol based liquids known as Ethaline. Particulate suspensions were formed by mixing silicon carbide (54-55 nm, hexagonal phase, Aldrich) with the appropriate ionic liquid (1 ChCl : 2 EG,) in wt./wt. % ratio. SEM and EDX elemental analysis was carried out under vacuum using a Philips XL30 ESEM instrument.

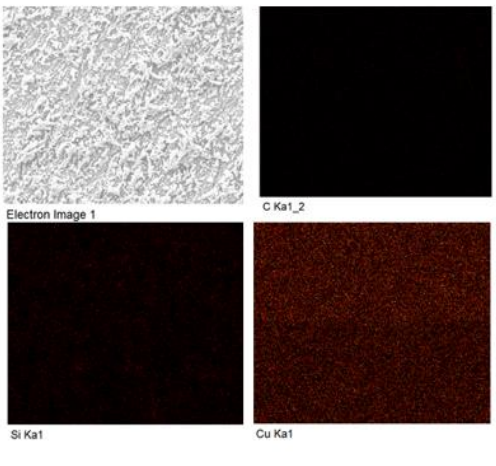
3. RESULTS AND DISCUSSION

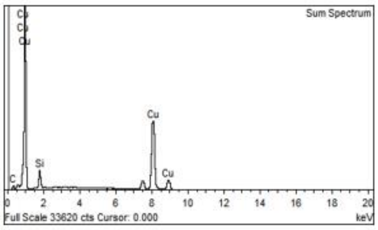
"Suspensions of various particulate materials including Si_3N_4, SiC, BN, Al_2O_3, and diamond can be formulated simply by stirring the powdered solid with the ionic liquid (DES). A key advantage of DESs for this application is that the particulate suspensions are stable over a prolonged period of time; this is presumably due to a combination of the increased viscosity (of the neat liquid), compared to water and coulombic screening of surface charge by the ionic liquid (high ionic strength)" [22]. Electrolytic deposition of copper films with and without SiC particulate of size 45-55 nm was used , the deposition carried onto nickel substrate. Using SEM-EDX to investigate the morphology of the surface of silver coating and the existence of the SiC particles.

It is proposed that this is a consequence of the increased free volume in the fluid component caused by the motion of the suspended particles i.e. the particles which act as tiny stirrers in the liquid. In this experiment we examine the surface morphology of copper deposites with and without second phase nanoparticles SiC (45-55nm) in the presence and absence of surfactants, where the two types of surfactant one sodium dodecylsulfate (SDS) Fig 2.a and the next one is hexadecyl trimethyl ammonium bromide (CTAB) Fig 2.b utilized. Both surfactants have shown remarkable interference in electrochemistry by the usage of the scanning electron microscope SEM-EDAX. The amount of SiC particulates in the composite coatings, which was determined using an energy dispersed X-ray microanlyzer (EDX) coupled to the SEM. Fig 1 shows that the deposited copper with the second phase nanoparticles is even and uniform, resulting in the roughness corresponded to loaded ceramic particles. Fig 1 shows that the hard phase loaded is higher than the mass loaded in the presence of both types in Fig. 2 which represents the added SDS, this is inconsistency; with the added soft second phase in the presence of SDS and CTAB surfactants [27]. The SEM and EDAX data represented in Fig 3 depict the substantial effect of CTAB surfactant on the mass loaded for both copper and nanoparticles, where the copper codeposited is reasonably less than the copper deposits without silicon carbide particulate, as shown by EdAX figures, which is not the case for the codeposition of soft material such as poly tetra fluoro ethane [27]. This has shown the appearance of gold peak, which can be seen from EDAX data in from EDAX data in

3.1 Copper Electrodeposited with SiC Nanoparticles without Surfactant

The presence of the second phase SiC 45-55 nm particle size is steady and moored during the time of codeposition of copper, this can be attributed to the fact that ethaline has a higher viscosity than water as well as ionic strength.





Element	Weight%	Atomic%
C K	6.97	27.10
Si K	4.91	8.16
Cu K	88.12	64.74

Fig. 1. SEM microstructure of copper co-deposits film with silicon carbide 45-55 nm size

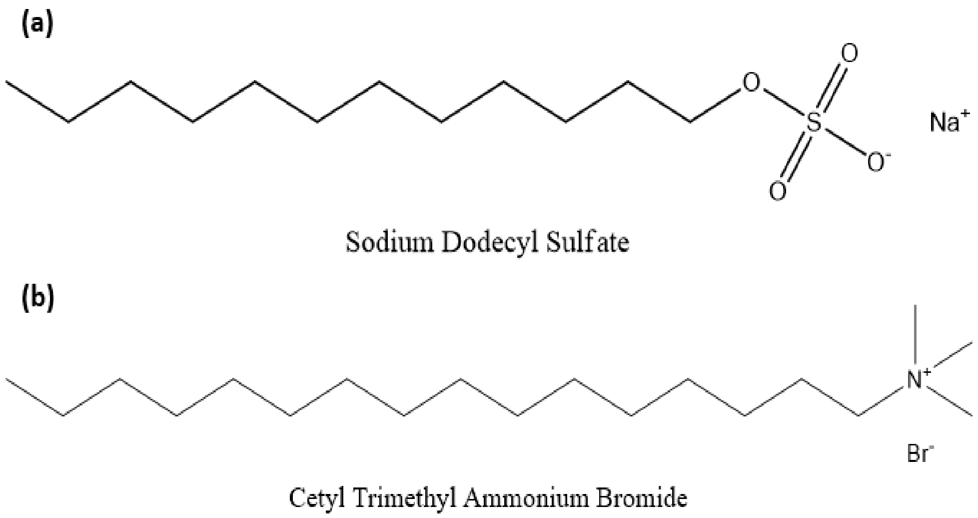
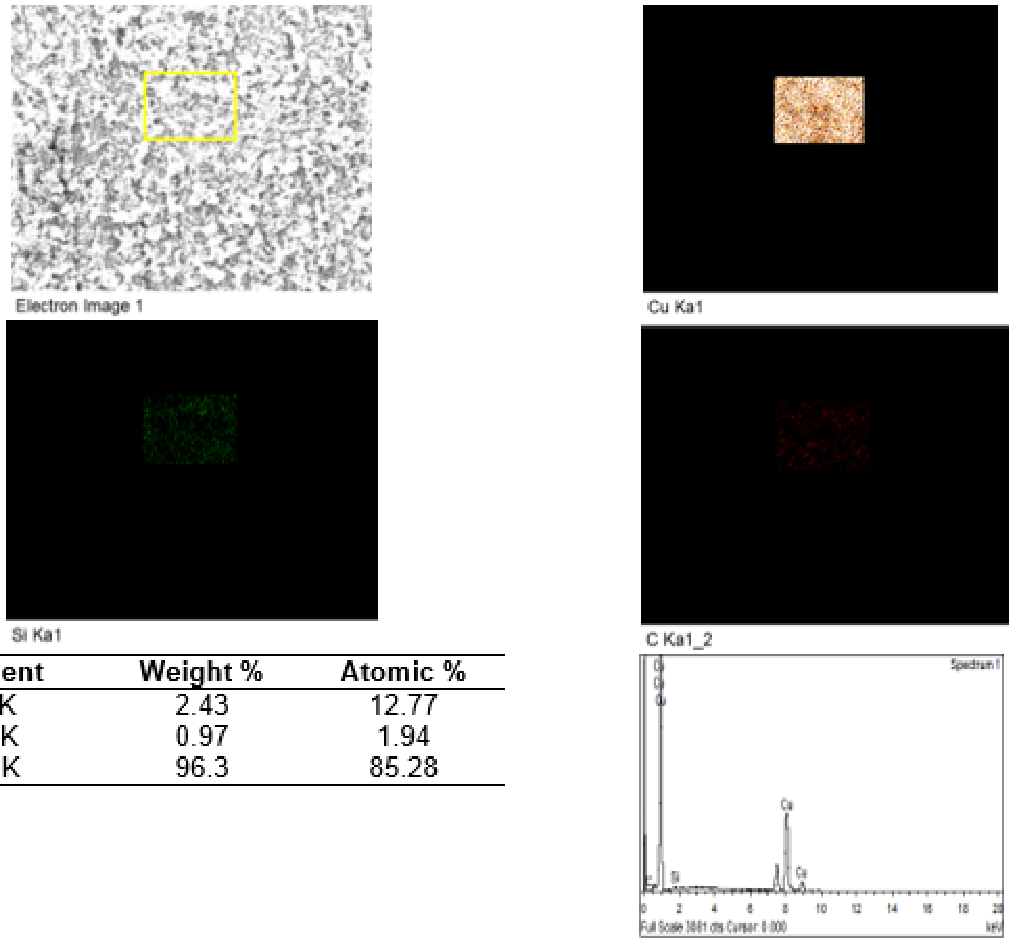
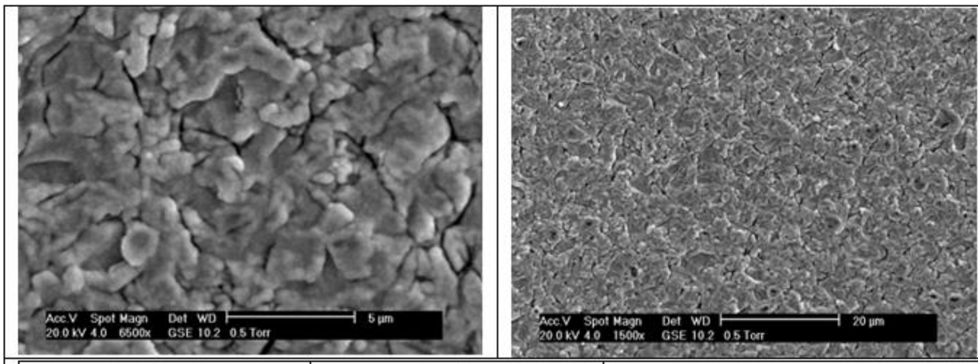


Fig. 2. Shows the two types of surfactants



Element	Weight %	Atomic %
C K	2.43	12.77
Si K	0.97	1.94
Cu K	96.3	85.28

Fig. 3. SEM micrograph of Cu electrodeposits with SiC nano particles from 0.1 M CuCl2, 1 mM SDS and 40 g / l SiC45-55nm in 1 ChCl: 2 EG based liquid at 0.8V and EDX map images show of Cu, Si and C in the copper coating



Elements	Weight %	Atomic %
C	2.37	13.81
Si	10.48	26.09
Cu	43.35	47.70
Au (substrate)	44.74	15.88

Fig. 4. SEM micrograph of Cu electrodeposits with SiC nano particles from0.1 M CuCl2, CTAB and 40 g / l SiC45-55nm in 1 ChCl: 2 EG based liquid at 0.8V and EDX map images shows of Cu, Si and C in the copper coating

3.2 Copper Deposits with 40g/L SiC 45-55nm Size in Presence of CTAB Surfactant

Long chain organic compounds is where one end is polar and the other end is nonpolar are used to minimize the surface tension between junction and accumulation into long chain structure. Unfortunately both types of surfactants showed a negative effect on the codeposition of copper. This requires further investigation.

Fig 4. Furthermore, the SEM images reveal the different surface texture with and without the two types of surfactants. This difference is attributed to the influence of SDS and CTAB on the rate of adsorption, aggregation and the mechanism of growthrate [27].

4. CONCLUSION

In this study, the electrodeposition of copper with hard second phase using deep eutectic ionic electrolyte (type III) reveals that both types surfactants have a negative influence on loading of the nanocomposites ceramics, on the other hand the SEM micrographs depict even distribution of SiC particulate irrespective of the presence/absence of the added surfactants, moreover it is interesting that the SEM images show the impact of the surfactants on the morphology of the electroplated copper with the dispersed phase.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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