Investigation of copper codeposits with SiC nanofrom Ionic Liquid (Ethaline) as function of concentration and micro particles sizes where the working electrode in 'Vertical' position using Acoustic Impedance Electrochemical Quartz Crystal Microbalance (EQCM)

ABSTRACT

The gravimetric inspection of co-electrodeposited copper, with hard inert second phase ceramics SiC and 0.02 M [$CuCl_2 \cdot 2H_2O$] in 1 ChCl: 2 EG, based liquid for different solution-phase loadings of 1-3 μm silicon carbide unpolished gold **AT** cut working electrode placed in'***Vertical***' position, revealed that the EQCM method admits the first *in-situ* quantification or particulate inclusion. It was found that the composition of incorporated substance was fairly dependant on the concentration of second phase particles in solution, where in this study the 5% SiC has the amount in the copper which is in a good agreement with alumina particles with the same size. Another observation was that most of the material was drawn onto the surface rather than settling on to it, howeverthe distribution of the hard phase was found to be reasonably even throughout the coating. This technology is important because it assists deposition of bright copper coatings without adding hazard materials, such as cyanide. On the other hand the comparison between concentrations of 0.02 M and 0.2 M[$CuCl_2 \cdot 2H_2O$] in 1 ChCl: 2 EG based liquid for 10% solution-phase loadings of 45-55 nm size silicon carbide was also investigated, where the working electrode is placed in'***Horizontal'*** postion.It is very interisting that the experimental result showed that the mass loaded by 0.2 M solution is about 10 times greater than for the mass loaded by 0.02 M solution.

Keywords: copper composites, ionic liquid, alumina, EQCM, working electrode vertical and horizontal positions, micro particles, nano particles, SiC and SEM.

INTRODUCTION

"The improvement of metal wear characteristics is an important topic in materials science. One methodology is to use composite coating.The electrodeposition of metal composites is relatively common and has been reviewed in detail"[1,2,3]. Most composite studies used nickel as a continuous metal matrix as it allows wear resistant coatings to be produced with a diversity of distributed phases. In the current study we focus on producing copper composites with improved hardness and wear resistance. Little work has been carried out in literature. Suzuki et al[4]studied "the co-deposition of aluminium oxide particles from an aqueous AgSCN bath". "It was concluded that the aluminium oxide particles adsorbed on the electrode and repressed Ag deposition. Two subsequent studies also investigated the co-deposition of submicron-sized titanium (IV) oxide particles with silver for the application as a photocatalyst. Titanium (IV) oxide was formed by the anodic oxidation of a titanium substrate rather than dragging titanium (IV) oxide particles from the solution"[5,6]. The only study to characterize the mechanical properties of silver composites was by Gay[7]et al. who studied"the inclusion of particulate zirconium (IV) oxide"."An alternative method of depositing metals is by using ionic liquids (ILs)".[8]"Silver coating has been explored by several groups as a model system for metal nucleation".[9,10,11,12,13]"They revealed that the inclusion of the composites materials in the plating bath alter and improve the surface coating morphology and lead to the hardness to increase from 88 Vickers (Hv) for pure silver to 140 Hv with 13.8% of zirconium (IV) oxide.In the this investigation we present that ionic liquids

based on eutectic mixtures of choline chloride and hydrogen bond donors such as ethylene glycol can be used as electrochemical solvents for the electrodeposition of copper. It was shown that coating the alumina grains with nanosized metal particles is a promising way to avoid the problem of heterogeneous distribution of the composites materials"[14,15,16]. "Such technique increases not only the evenness of the coated area but also the mechanical properties of ceramics. In this paper, we present a wet-chemical method to coat Cu nano-sized particles on silicon carbide grains uniformly.. The microstructure and mechanical properties of the silicon carbide/Cu ceramic were analyzed and discussed. We have used an electrochemical techniques EQCM, andwith scanning electron microscopy to characterise these systems. Composites of copper with silicon carbide have also been produced. Wereveal that the proportion of these species incorporated into the resulting electroplated films is determined by the mass loading in the solution. The main process for particulate involvement is caughtonto the electrode surface. The inclusion of second phase particle in the liquid is found to have insignificant effect upon the fluid viscosity of the suspension; this can suggest to a consequence of the growing free volume in the fluid component generated by the movement of the suspended particles *i.e.* the particles work as tiny stirrers in the liquid. In previous research we have electrolytically deposited copper composites from DESs and quantified the incorporation of alumina of different particle sizes"[17].The electrical current is used electrolytically to deposit copper composite films on a working electrode in **vertical** and **horizontal** positions and investigate the amount of deposited silicon carbide in the copper coating and the thickness as a function of both size of incorporated particulates.SiC (45-55nm and 1-3μm) composites on gold substrates are compared. We use SEM to investigate the morphology and composition of the coated surface and show the existence of ceramic particles.

METHODOLOGY

Choline chloride [$HOC_2H_4N(CH_3)_3Cl$] (ChCl) (Aldrich 99%) wasused and received, when necessary, recrystallised from absolute ethanol, filtered and dried under vacuum. Ethylene glycol (EG) (Aldrich 99+%), was used as received. The mixtures were formed by stirring the two components together, in the stated proportions, at 50 ^oC until a homogeneous, colourless liquid formed). The liquids, once formulated, were kept in a thermostatic oven at 50 ^{o}C prior to use. Particulate suspensions were formed by mixing either Al_2O_3 (0.05μm or 1.0 μm, Aldrich), Aldrich) with the appropriate ionic liquid (1 ChCl : 2 EG, in wt./wt. % ratio.

"Acoustic impedance electrochemical quartz crystal microbalance (EQCM) experiments were carried out using electrodes consisting of thin Au films(no Ti or Cr binding layer was used) evaporated on 10 MHz AT cut quartz crystals (International Crystal Manufacturing Co., Oklahoma City, USA); the surface finish of these crystals was unpolished. The piezoelectric active electrode area was 0.23 cm^2. Crystal impedance spectra were recorded using either Hewlett Packard HP8751A network analyser, connected to a HP87512A transmission / reflection unit via 50 Ω coaxial cable (or an Agilent ENA E5061A network analyser) such that the centre of the spectrum was near the centre of resonance, f_o(10 MHz), with a typical sweep width of 20-200 kHz depending on the interface. Peak frequency/mass, ***Q***factor data were extracted from the acoustic impedance spectra by fitting to a Lorentzian line shape using methods described elsewhere"[18,19,20].

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RESULT AND DISCUSSION

An electrochemical quartz crystal microbalance, EQCM, was used to determine charge / mass balance for copper codeposition with second phase silicon carbide nano and micro sizes and a representative data set is presented, were placed in vertical position vertical.

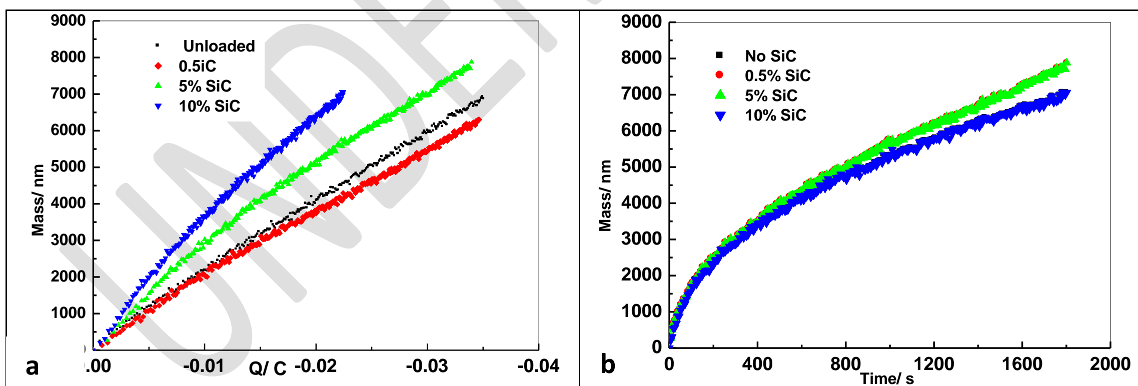
EQCM analysis of codeposited copper with (1-3μ)silicon carbide (working electrode on vertical)

UNDER PEER REVIEW

Electrochemical quartz crystal microbalance assessments were utilised to attain the mass loaded versus the charge plots for copper deposition with two different sizes of silicon carbide 1-3μm suspended in the ionic liquids. This method employs and allows real time *in-situ* in observing, of both the copper deposition rate and the inclusion of silicon carbide (or any particulate) built into the composite. Since the second phase adds to the mass without using up a charge, where the place of AT cut working electrode was changed from the horizontal to **vertical** position, which is significant as it can inscribe the matter of whether the composite material is settling on the surface or being dragged there by the copper complexes. The liquids were all kinetically stable on the time scale of the experiment i.e. the silicon carbide did not lay out at any time during the experiment, and thisshows that the sedimentation of the second phase is doubtful to be a decisivepartner to the overall rate of the material incorporation.**Figure 1a**represents the loaded mass versus charge graph for copper at -0.8 V for 0.5%, 5% and 10% solutions phase loadings of 1-3 μm silicon carbide in 1 ChCl: 2 EG based liquid (ethaline).**Figure 1b**shows inconsistency with the same amount of alumina micro particle added to the copper codeposits with the same parameters[21] , where the 10% of silicon carbide micro particles has more current efficiency than 10 % alumina 1μm particle size,It can be seen that thecurrent is significantly reduced when a high concentration of particulates are added to the solution. It is most likely that the attenuation of the current response is caused, by physical blocking of the working electrode surface by the insulating particulate mass *i.e.* effectively decreasing the conducting electrode surface area. In this study the difference between mass loaded between alumina and silicon carbide, could be attributed to the in density where alumina has higher density than silicon carbide, so it sediments faster. furthermore mass loaded with incorporated silicon carbide is between 7.0×10^{-6} g and 8.0×10^{-6} g ,while mass loaded with incorporated alumina micro particles in the range about 1.1×10^{-5} g loaded which is in a goodagreement according to the amount of ceramics loaded in the solution (5%). It is interesting that the thickness of the copper codeposits is shown in **Figure 1c**indicates that the maximum thickness is represented 5% SiC(4.7 micron) particles, this is less than the thickness obtained by copper codeposits obtained by alumina particle (5%) , where the coating thickness is about 8.0 micron.**Figure 1d**, where Q is the bandwidth and the resonant frequency determines the quality factor.

The scanning electron microscope micrographs displayed a considerable result of incorporating silicon carbide micro particles; on the morphology of the deposites, the quantity of silicon carbide, this is consistent with theresults by codeposition of dispersed phase of alumina (nano / micro particles) and soft second phase particles poly tetra fluoro ethylene versus the deposition of pure copper, some mechanical properties, such as hardness, and wear properties were investigated[22, 23] One of the benefits of ionic liquidsis mentioned above, is the capability to deposit metals onto surfaces that usually inert or aresusceptible to water. **Figure 2.a, b, c and d** show aSEM micrograph of a copper/ Silicon carbide composite obtained from the electrodeposition of potential applied 0.8V for 30minutes at room temperaturehave even distribution of second phase particle and the incorporated particles of silicon carbide is dragged to the surface rather than settling. However, it should be noted that the comparison of SEM micrographs of copper with and without SiC particles produces coatings with different surface textures[22].

UNDER PEER REVIEW



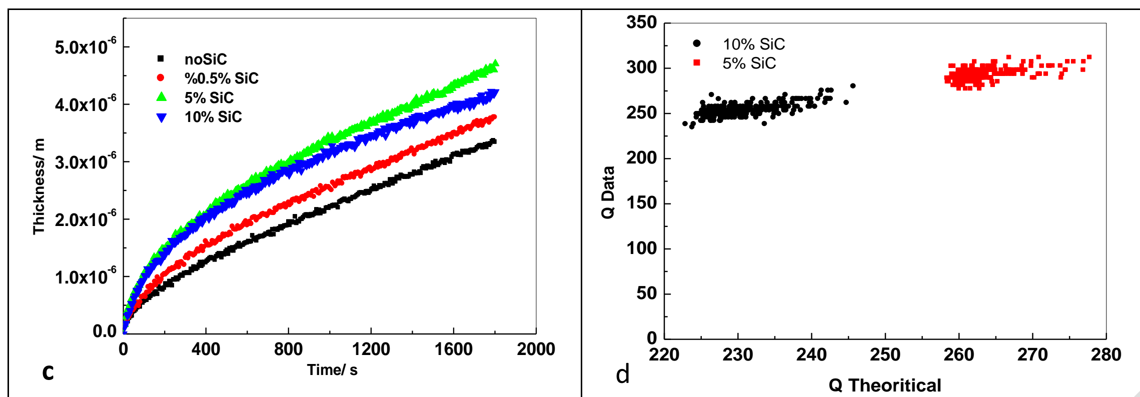


Figure 1. Mass-charge graphs for copper codeposition at -0.8 V and 0.02 M [$CuCl_2 \cdot 2H_2O$] in 1 ChCl: 2 EG based liquid for different solution-phase loadings of 1-3 µm silicon carbide.

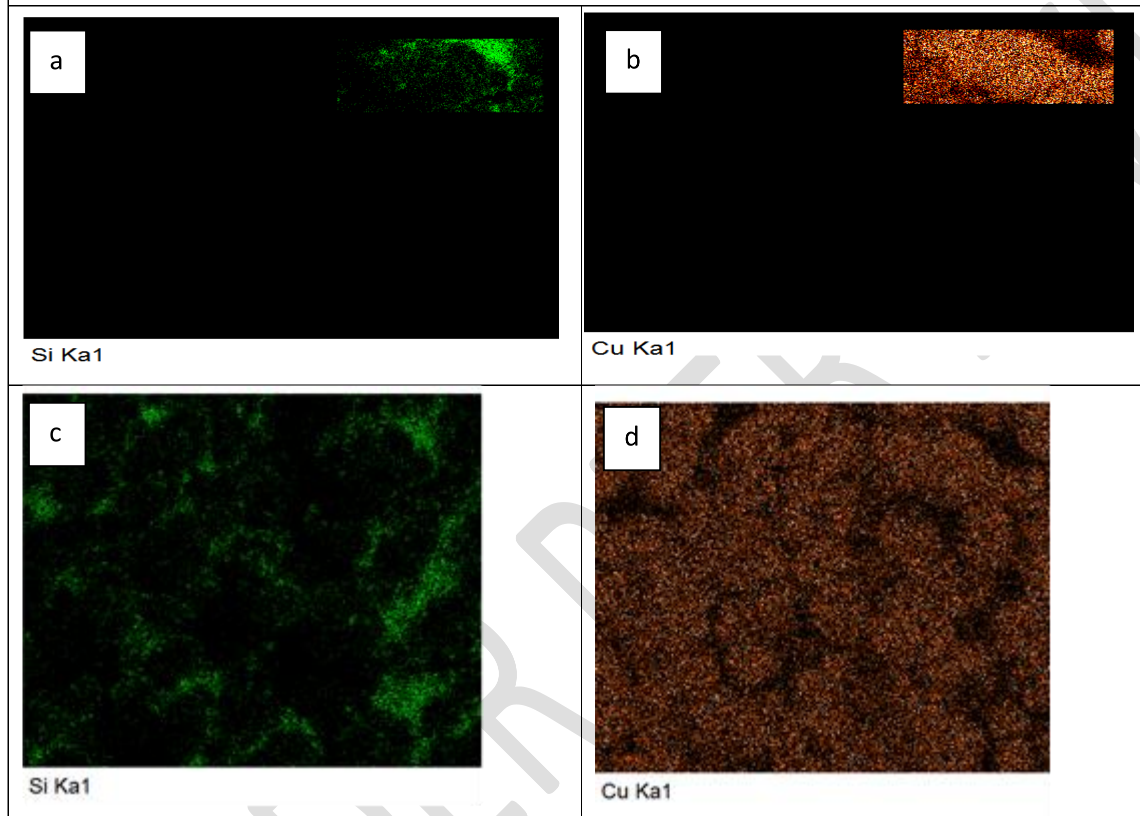


Figure 2.SEM micrograph of copper codeposites incorporated dispersed phase of silicon carbide 10% 1-3µm silicon carbide. . Deposition at -0.8 V and 0.02 M [$CuCl_2 \cdot 2H_2O$] in 1 ChCl: 2 EG based liquid.(**vertical position**).(scale bar 5µm)

Gravimetric studies on the effect of copper concentration on codeposition composites of SiC 45-55nm particles (working electrode in horizontal position)

Copper has been electroplated from numerous ionic liquids; in the period of 1960s to1970s the investigation of these procedures was influenced by chloroaluminate ionic liquids. [24,25,26,27] With the prelude of discrete anions such as $[BF_4]^-$,and $[(F_3CSO_2)_2N]^-$ ($[Tf_2N]^-$) in the 1990s, copper is feasiblemore bysimply electrodeposited and the air and moisture stability of these systems.[28,29]This is important as it can address the issue of whether the composite material is settling on the surface or being dragged there by the copper complexes. The liquids were all kinetically stable on the period time of the analysis *i.e.* the silicon carbide nano particles did not settle out at any time during the experiment and this suggests that the sedimentation of SiC is uncertain to be involved to the overall rate of material inclusion[22].The effect of the size and the

UNDER REVIEW

concentration of alumina were discussed. Now the concentration was kept constant (10 % w/v) of 50 nm size while the concentration of Cu ions was varied. Surprisingly **Figure 3.a** and **b**depict that the amount of embodied silicon carbide in the Cu co-deposits is not fairly the same,which is not the case for alumina with the same particlesdirecting that the amount of incorporated ceramics is uninfluencedby copper concentration as well as the time range for Cu concentrations. It has been noticed that the film deposits from 0.2 M(***7.3x 10^{-5} g***) Cu solutionis **10.3** times larger than deposited from 0.02 M Cu(***7.1x 10^{-6} g***) solution.**Figure 3.c**presentedmass loaded of copper and the ceramics silicon carbide as function of time, for half an hour which is consistent with the mass loaded as function of charge. The colloidal solution is observed stable during the course of the experiment, which is shown in **Figure 3.d**. The thickness of copper codeposition (**Figure 3.e**) is calculated from both copper solution concentration from **Figure 3.a** and **Figure 3.b**, this is very interesting in the industrial scale that the thickness of copper coating with incorporated particles can be controlledwith the required width. The mass of the electroplatedcopper from both solution concentration (0.02M and 0.2M solution) with second phase silicon carbide as function of current density is observed in **Figure 3.f** , shows most of the current is consumed on the codeposition of copper with second phase nano particles.

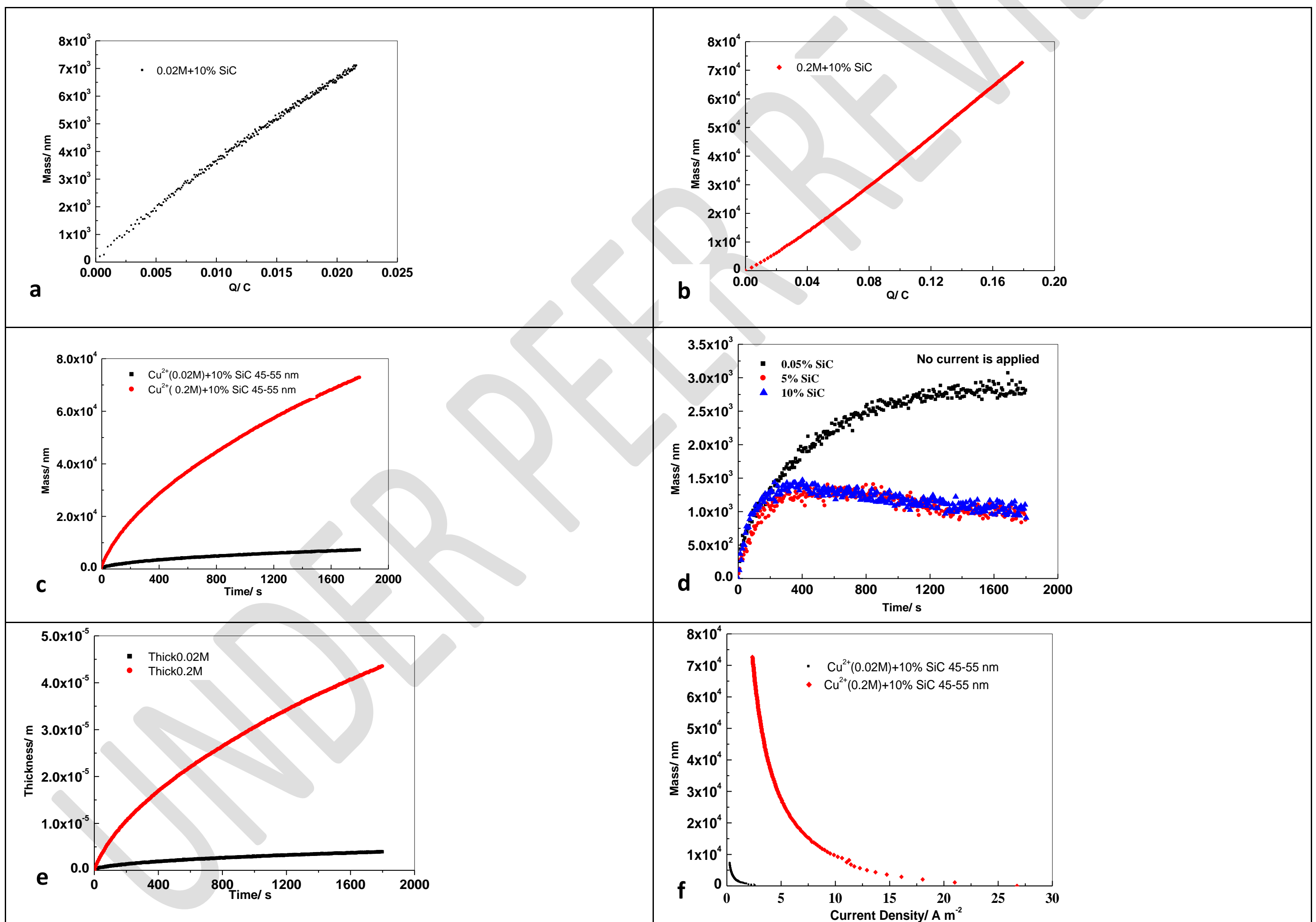


Figure 3.Mass-charge plots for copper deposition at an applied potential of -0.8 V of [$CuCl_2.2H_2O$] concentrations between0.02 M and 0.2 M but with constant solutions second phase loading (10 wt. %) of 45-55nm SiCin 1 ChCl: 2 EG mixture .

UNDER PEER REVIEW

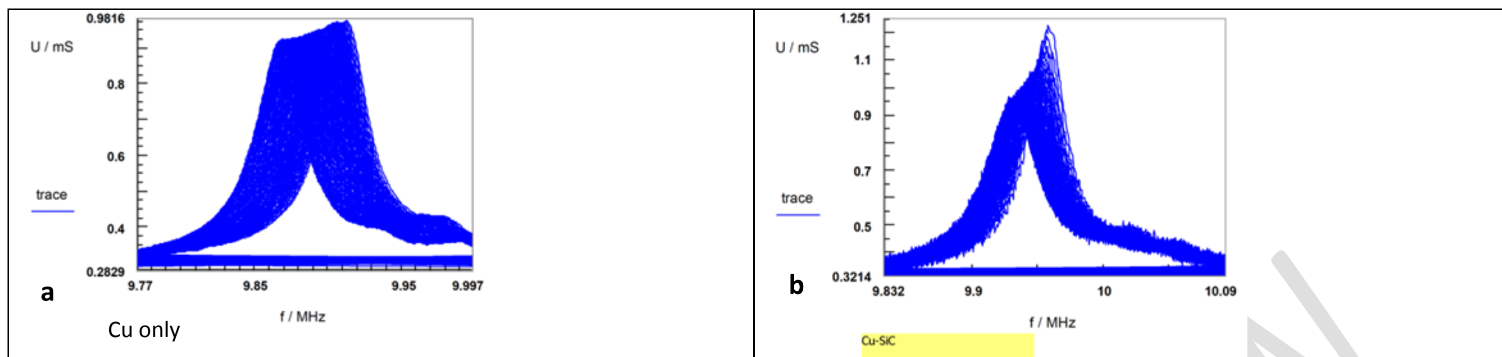


Figure 4.frequency (**f_0**) is plotts against attmedance (**U**)for unloaded copper only (a) and loaded copper with ceramics (b) at an applied potential of -0.8 V of [$CuCl_2.2H_2O$] 1 ChCl: 2 EG mixture .

Raw spectrum data are fitted to the Lorentz line shape using XL macros to extract the centre frequency, f_0, the peak intensity, and the peak shape. Frequency can give information about the mass. Shape, broadness, can give information about the surface of the crystal. In **Figure4aand b** show frequency (***f_0***) is plotts against attmedance(**U**)for unloaded copper only and loaded copper with ceramics, which interprete the even surface texture[30] but a little noise can be seen in codeposition of copper codeposits in **Figure4.**

CONCLUSION

This work shows that the ionic liquids, based on eutectic mixtures of choline chloride and hydrogen bond donors, such as ethylene glycol, can be utilized as electrolytes solutions for the electrodeposition of copper. The research explained that in an ionic liquid, the current efficiency for copper deposition is moderately efficient when **AT** cut working electrode is placed in a **vertical** position. Copper, incorporated with silicon carbide, has also been produced and shows that the loading of these species in the resulting electroplated films is not dependent on the concentration of particulate in a solution. When the working electrode is located vertically, it was found that 5% of inert hard ceramics is the most loaded in the codeposits film. In another experiment, however,the particulate of silicon carbide 45-55 nm size loading was kept constant, at 10% and the concentration of Cu ions varied from 0.02 M to 0.2M.Here all the mass-charge plots are again linear, confirming that the uniform distribution of particulates throughout the coatings.Two copper concentrations solutions are essentially identical, indicating that the Cu: Sic ratio is the same in each of the depositions despite the fact that the higher Cu concentration resulted in a tenfold increase in the amount of copper deposited. Gravitational settlement has been excluded as the main mechanism for particulate inclusion into the electrolytic deposits, due to the position of the working electrode. It is surprising that the deposition of copper incorporated with nano particle alumina is fairly dependent on the concentration of silicon carbide. It has observed in previous study[21], the inclusion of micro alumina particles showed that 5% is the highest loading in the deposit, which is a very interesting observation.

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UNDER PEER REVIEW

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