PLATING FROM IONIC LIQUIDS-
JUST A GOOD IDEA OR A CHALLENGE FOR ELECTROPLATING?

C. Werner[1], A. Moebius[1], A. Koenig, F. Endres, G. Zeng, R. Pittner
[1]Enthone GmbH, Langenfeld, Germany
[2]Univ. of Erlangen-Nuremberg, Germany
[3]Univ. Clausthal-Zellerfeld, Germany
[4] Aachen, University of Technology
[5]Merck KGaA, Germany

ABSTRACT

In the last few years a new generation of electrolytes came into the focus of electroplating industry. These systems do not contain any water and consist only of salts: Ionic Liquid (ILs). An ionic liquid is a liquid that contains essentially only ions and usually show melting points below 100°C (212°F). Some ionic liquids have an electrochemical window of 3-5 Volts which make them attractive for plating processes (such as chromium, aluminium, magnesium, titanium & others) [1]. A lot of international R&D groups at universities work in the field "Plating from Ionic Liquids". It could be shown that chromium, aluminium, selenium, magnesium & tantalum could be plated from these type of solutions. However it turned out that the implementation into an industrial process is not that easy because most of the ILs or metal salts are highly humidity or air sensitive. In this report we show the opportunities but also the difficulties using IL-technology for plating application. It will discuss applicability and market.

.

INTRODUCTION

Common electrolytes for plating industry basically consists of metallic or semi-metallic ions, some organic additives and water as solvent. For special application (such as plating of aluminum) organic solvents are used. In the last ten years a new class of solvents became into focus of electrochemistry: Ionic Liquids. Ionic liquids represent a new class of salts that are distinguished by a range of useful properties such as negligible vapour pressure, thermal stability, no flammability, high ionic conductivity and remarkable solubility properties. Most of the ILs consist of at least one huge ion such as 1-Butyl-3-methylimidazolium that obstruct crystallisation and so stay liquid.

For plating industry especially the large electrochemical window and big working temperature range is interesting.

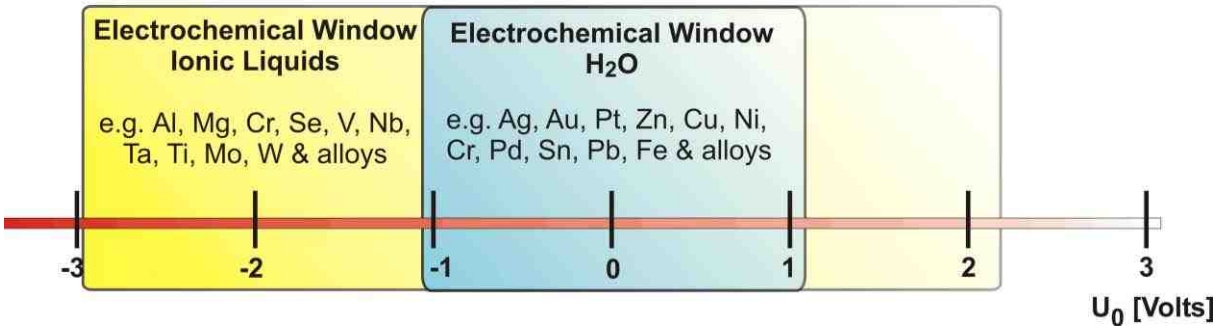

Figure 1: Electrochemical window and broad working temperature range of ionic liquids

Generally an Ionic Liquid based plating system would allow to plate refractory metals like aluminium or titanium which would be highly interesting for wear- and corrosion resistance.

ALUMINUM PLATING FROM IONIC LIQUIDS

One of the most interesting materials to plate from Ionic Liquids is aluminium for corrosion protection. recent papers report on the electroplating of mild steel by aluminium in a first generation ionic liquid [EMIm]Cl/$AlCl_3$ (40/60 mol.-%). The study was performed by means of cyclic voltammetry and galvanostatic polarization complemented by SEM/EDAX and optical microscopy[2]. The second generation of ionic liquid allow to plate in an oxygene containing atmosphere (e.g. [EMIm]Tf_2N + 5.5 mol/L $AlCl_3$, Figure 2).

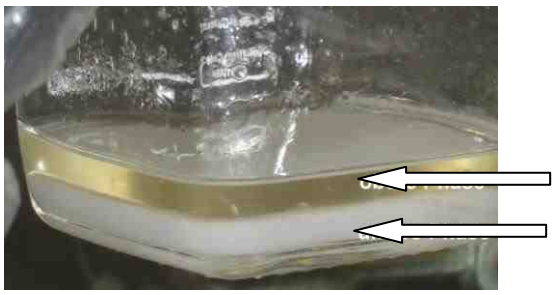

Figure 2: Mixture of [EMIm]Tf_2N / $AlCl_3$

]

The results show that the pre-treatment of the substrates plays a key role in the coating adhesion. The substrate has to be activated well by an anodic dissolution of the iron oxide layer and the subsequent re-deposition of iron or Fe-Aluminium alloy formation prior to Al bulk deposition. Some plating results are shown in figure 3.

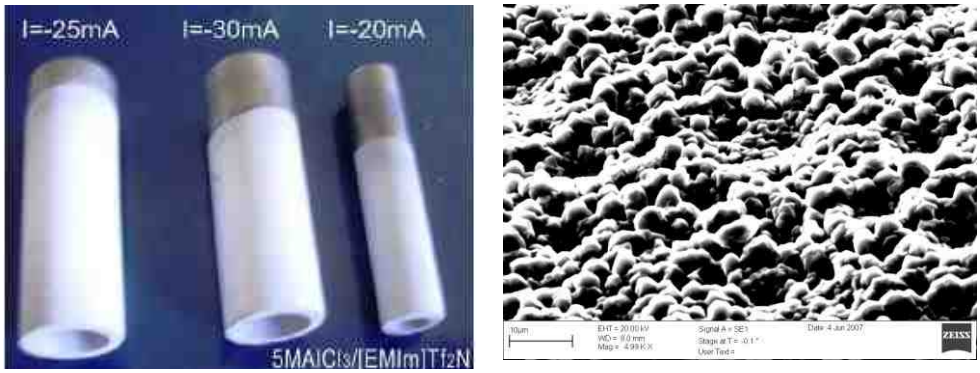

Figure 3: Aluminium plating on mild steel pipes (left), microcrystalline structure (right)

The Al-deposit shows a uniform microcrystalline structure. The coverage is good and the corrosion protection properties are outstanding. By changing the formulation slightly the appearance of the deposit changes from matt to semibright.

CHROMIUM PLATING FROM IONIC LIQUIDS

A chromium top coat is one of the most used finishes in plating industry. Up to now the major plating is performed by using chromium(VI) for generating thick chromium layers. Electrolytes based on Cr(III) are sometimes an alternative but unfortunately they can not form thick Cr-layer with an acceptable hardness. The use of ionic liquids can be an alternative [3]. It could be shown that chromium can be plated by a cholinechloride (vitamin B4) containing electrolyte. The deposited layer is black. Other Ionic Liquids show similar results. But during the experiments it turned that the anode question has to be solved. Inert anodes such as platinised titanium is not suitable because they are dissolved so that not only chromium is plated – a Cr-Pt-alloy results.

SELENIUM PLATING FROM IONIC LIQUIDS

Furthermore, the electrodeposition of Se in the 1-butyl-1-methylpyrrolidinium bis(trifluoro-methylsulfonyl)amide ([BMP]Tf_2N) has been demonstrated[4]. Selenium is one of the most interesting materials for solar cell application. A new type of flexible thin film photovoltaic cell – called CIGS or CIS – need selenium for semiconductor formation. The high thermal stability of the ionic liquid as well as the large electrochemical window of this ionic liquid compared with aqueous electrolytes allow the direct electrodeposition of grey selenium. The results show that grey selenium can be obtained at temperatures ≥100 °C.

PLATING FROM IONIC LIQUIDS SOLUTION: NEEDS & CHALLENGES

As could be shown in the chapters above a lot of potential elements are waiting to be plated from an Ionic Liquid solution. But for achieving this goal certain points have to be considered:

- the plating system will be expensive. Small reactors and selective plating cells have to be developed. One opportunity is a plating robot that works in a controlled atmosphere.
- the anode question:. If the use of soluble anodes is not possible common insoluble anodes can not be used easily because they may be destroyed because of the broad electrochemical window.
- new generations of additive packages have to be developed, replenishment concepts such as dialysis have to be adapted.
- the solvent itself has a certain value. Certainly, with up-scaling the production the Ionic Liquids become cheaper. Nevertheless they will never be as cheap as water. Therefore a recycling and rejuvenation concept has to be developed.

Figure 4: Concepts for using Ionic Liquids as a matrix for plating

SUMMARY AND CONCLUSION

Ionic Liquids that are used as solvent for plating industry offer the possibility to win new markets for electroplaters. Aluminium and refractories as well as silicium or selenium can be deposited from an Ionic Liquid based system. The broad electrochemical window and the large temperature range makes it possible. The Ionic Liquid system can be adjusted for each plating system specifically. A huge amount of different ILs are available and will be developed in the future. Certainly there are a lot of challenges that the user has to deal with: New anodes, new additive system, single reactor technology and in-situ recycling/regeneration and especially the high price of the ILs itself will slow down the development. But the potential is still huge. ILs are a high potential high tech application for electroplating industry with high value which will not be easy to copy.

ACKNOWLEDGEMENT

Some of this work presented here was performed within the project INNOSURF by the german ministry of research & development and by the IONMET project funded by the european union. The author would like to thank these institutions and the co-workers for the support.

LITERATURE

[1] T. Tsuda and C. L. Hussey, “Electrochemistry of Non-Chloroaluminate Room-Temperature Ionic Liquids,” in *Modern Aspects of Electrochemistry*, (2007).

[2] Q. X. Liu, S. Zein El Abedin, and F. Endres, Electrodeposition of Nanocrystalline Aluminum: Breakdown of Imidazolium Cations Modifies the Crystal Size, J. Electrochem. Soc 155, 5 pp. D357-D362 (2008)

[3] http://www.ohlsti.co.uk/ohl/stipdfs/ohl_sti32.pdf

[4] Patent WO/2007/039035