Recent Developments in the Field of Aluminum Deposition Using Ionic Liquids

A. Alemany,[1] I. Malkowsky,[1] U. Vagt,[1] M. Maase[2] and M. O'Meara[2]*

[1]*BASF SE, D-67056 Ludwigshafen, Germany*
[2]*BASF Corporation, Florham Park, NJ, USA*

Having gained great interest over the years, ionic liquids are currently being evaluated as valuable alternatives for use in many commercial processes and products because they provide novel solutions that cannot be achieved with other materials. This paper addresses applications using ionic liquids that have been commercialized, or that are close to commercialization, especially within the field of metal processing. It specifically addresses achievements in aluminum deposition from ionic liquids for use in surface finishing applications as well as the corrosion protection behavior of these galvanic aluminum coatings.

Keywords: *Aluminum deposition, non-aqueous electrolytes, ionic liquids*

Introduction

Surface coating is of major importance technically as well as economically. Surface finishing processes are used not only in classic fields like mechanical and plant engineering, aircraft and spacecraft, automotive and medical technology, but they are a key technology in many other industries as well. The application of functional coatings can modify the properties of material surfaces, for example, their hardness, roughness, chemical resistance or wettability, to adapt them to the specific technical requirements they must meet. Of special importance in this respect is their protection against corrosion and wear and tear.

The current state-of-the-art electroplating processes that are used to produce metallic surface coatings are based mostly on electrochemical deposition of metals from aqueous electrolyte solutions. However, reactive metals like aluminum and aluminum alloys cannot be deposited by these traditional techniques because the electrochemical window of aqueous electrolyte solutions is too narrow. Water begins to decompose, forming hydrogen and oxygen, before [redacted]

[redacted] megan.omeara@basf.com

While this vacuum-based metal-coating process allows for a broad range of materials to be deposited by means of vapor, including aluminum, its deposition rate is low which implies poor space-time yield and requires investment in expensive plants and equipment. In the late 1950s, Ziegler and Lehmkuhl[1] developed an alternative electroplating process using alumino-organic compounds. The major drawback of the process was that handling these compounds is extremely difficult because they are both sensitive to humidity and air as well as being pyrophoric and self-igniting. It was therefore necessary to invest in additional safety devices to guarantee safe industrial-scale processes.

Recently, BASF Group, based in Ludwigshafen, Germany, developed a new lab-scale process that is based on the use of ionic liquids and offers a range of advantages over traditional methods. First, it allows for faster aluminum deposition; second, the system can be easily and safely managed; and third, it is cost-efficient because the ionic liquid is captured and recycled.

The metal coating applied in this way adheres exceptionally well to the substrate and is both solid and homogeneous. Moreover, its finish quality is attractive. A crucial benefit of the ionic liquid process is that it does not require any major changes in the flow of established electroplating processes. It is actually a new process made up of mostly well-known process steps.

Ionic liquids are salts that are liquid at low temperatures due to their chemical structure, comprised of mostly voluminous, organic cations and a wide range of anions. These liquids consist solely of ions. They do not contain any other non-ionic components like organic solvent or water. In a way, liquid salts combine the properties of solids and liquids in a single material, resulting in unique characteristics and physical properties that no other material achieves. These distinctive characteristics facilitate many innovative solutions in terms of processes and products, some of which have already been successfully established. In fact, as early as 2003, BASF had effectively applied these liquid salts for the first time in a commercial chemical process.** Building upon this success, BASF collaborated with customers to develop additional applications that use ionic liquids as electrolytes. Yet another focus currently in development is a process that utilizes ionic liquids to dissolve and reshape cellulose. The process, described here, for the electrodeposition of aluminum, adds another new field of application to BASF's portfolio.

The new aluminum deposition process consists of three individual steps as shown in Figure 1. First, the substrate is cleaned, degreased and pickled, as in a classic pretreatment process.

However, as opposed to classic electroplating methods, the substrate is then dried. Second, the electrodeposition step that uses ionic liquid as its electrolyte is carried out. To achieve high ion mobility and a high deposition rate, the process is run at temperatures ranging from 60°C to 100°C. The aluminum that is deposited in this process comes from the aluminum anode, while the substrate serves as the

** *BASIL™ Ionic Liquid Process (Biphasic Acid Scavenging Utilizing Ionic Liquids), BASF Corporation, Florham Park, NJ 07932.*

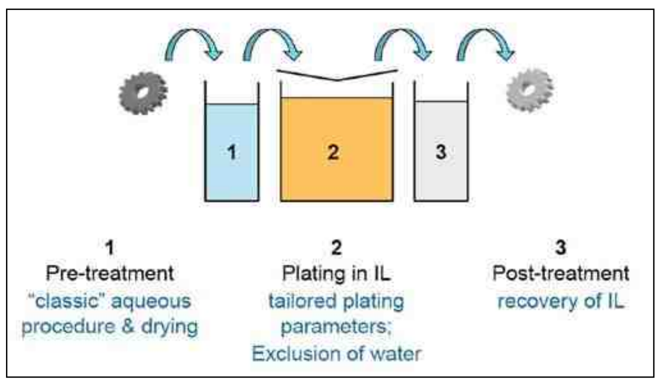


Figure 1 - Aluminum deposition process from ionic liquid electrolyte solution.

cathode. In all cases, the deposition, which occurs at a fast rate, results from chloroaluminate complexes that are formed as intermediaries. In contrast to processes using alumino-organic compounds, which require a stringent separation from atmospheric oxygen and moisture, this type of aluminum coating process requires only simple precautions to ensure that moisture is largely excluded. The system remains stable up to a water content of 0.1 percent by weight. At higher water content however, the electrolytic bath does form interfering aluminum oxychloride compounds and undesirable hydrochloric acid vapors. Nitrogen gas is therefore used as a protective "blanket" to prevent water from being introduced into the system, thereby suppressing the formation of these undesirable by-products.

The electrolyte is based on 1-ethyl-3-methyl imidazolium chloride (EMIM Cl) ($C_6H_{11}ClN_2$), a product that is currently available on an industrial scale. Special, and expensive, purification of the basic electrolyte is unnecessary. By contrast, the choice of additives used with the basic electrolyte is decisive, where specifically 1.5 molar equivalents of aluminum chloride are used along with other additives.

The coating grows at a speed of up to one micron per minute and forms a solid film with varying thickness and quality that is dependent upon the additives in the system. For example, deposition from an additive-free electrolyte produces dendrite-like structures that have poor adhesion, lack solidity and do not produce a good quality finish (Fig. 2a). Inclusion of these proprietary additives ensures that the film deposited is free of dendrites, highly solid and adheres superbly to the substrate (Fig. 2b). In addition, the coatings resulting from this process are distinguished by excellent finish quality and achieve these excellent results without incorporating the additives into the coating. Substrates coated in this manner may include a range of metals like copper, iron, steel or nickel.

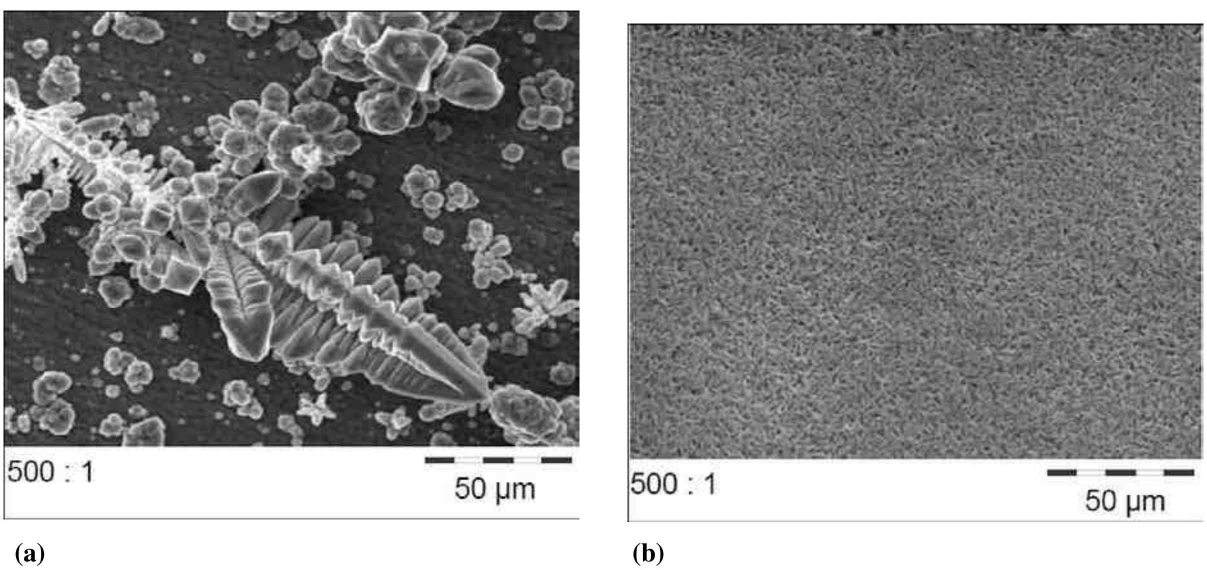


Figure 2 - Aluminum deposited from EMIM Cl × 1.5 $AlCl_3$: (a) pure solution without proprietary additive; (b) with proprietary additive.

Finally, the third step of the process consists of finishing the work piece that has been coated. First, any ionic liquid still clinging to the workpiece is removed and recycled back into the electrolytic process. The aluminum surface is then passivated if necessary and further modified as required. Mechanical polishing, for example, will turn the aluminum coat into a top-quality high-gloss surface with a mirror finish.

In summary, BASF has developed an aluminum deposition process that combines a number of advantages:

- Standard pre-treatment procedures,
- Current density range from 400 to 800 A/m^2 (37.0 to 74.1 A/ft^2),
- Electrolysis at less than 100°C,
- Use of a robust electrolyte system that tolerates up to 0.1 wt% of water, and
- Minimal loss of ionic liquid.

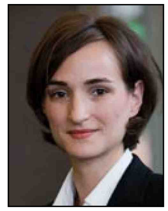
The appeal of the new process lies in the high purity and density of the aluminum coating it produces, in the excellent adhesion between the coating and the substrate, and in the options it offers for modifying the surface finish.

BASF is positioned to help its customers to actively develop and implement processes for the deposition of aluminum from ionic liquids on a number of substrate materials. This assistance can include supply of the electrolyte along with advice on how to handle ionic liquids and/or design of a customer specific electrolytic process.

Reference

1. K. Ziegler & H. Lehmkuhl, "Die Elektrolytische Abscheidung von Aluminium aus organischen Komplexverbindungen," *Zeit. Anorg. Allg. Chemie*, **283** (1-6), 414 (1956).

About the Authors



Ms. Aurelie Alemany is New Business Development Manager Ionic Liquids at BASF SE, Ludwigshafen, Germany. She holds a Chemical Engineering degree from Ecole Supérieure de Chimie de Nancy, France (1999) and an Executive MBA from Essec Paris & University of Mannheim (Germany). She joined BASF in 1999 as a Process Engineer and worked her way to her current position, which she has held since 2007. Her work focuses on the development of sustainable technologies to improve the recovery of waste heat and the development of electrodeposition processes of aluminum.

Dr. Megan O'Meara, is New Business Development Manager – Ionic Liquids for BASF Corporation, Florham Park, NJ. She holds a Bachelor's degree in Chemistry and Sociology from the University of Arizona (2000), and a Ph.D. in Chemistry from the University of Alabama (2005) under Dr. Robin Rogers studying the effects of ionic liquids on protein stability and activity. Her current interests include the use of BASF ionic liquids and ionic liquid technologies throughout various industries for a wide range of applications and specifically to promote electrodeposition processes of aluminum for corrosion protection and/or decorative applications.