Novel Materials and Products From Anodised Aluminium

Introduction
Electrolytic processing (or anodising) of aluminium can generate a porous surface oxide film of precise morphology where sub-micron cells extend perpendicularly from the surface in a regular array. Such anodic oxide films can be used as templates for replicating organic and inorganic species with features on a sub-micron scale. This approach has been reported widely in the literature for potential applications as diverse as optoelectronic and magnetic storage arrays, multi-gram synthesis of metal nanowires, nano fuel cells arrays, and the growth of vertically aligned and isolated carbon nanotubes (CNT) or fibres. In general such developments employ pore-filling techniques such as electrodeposition or chemical vapour deposition. The electrolytic processing of aluminium can therefore be considered as a platform technology for a range of replicate product opportunities, potentially offering a lower cost alternative to competing replication technologies but with the additional prospect for larger area manufacture. This article reviews technology developments in the field and discusses a high market value opportunity in pressure sensitive adhesive tape products.

Aluminium anodising
Figure 1 shows a schematic representation of an anodic film grown on an aluminium substrate by electrolytic processing. Typically, such films are ~20 μm thick in total although thicker or thinner films may be grown by control of the anodising conditions. The pore diameters typically range from ~10-200 nm, depending on the process conditions and electrolytes employed and the pore population density is in the range of $10^7 - 10^{11}$ cm$^{-2}$. Note that, at the base of each pore, a “barrier” aluminium oxide film extends in a contiguous fashion across the aluminium metal substrate. The chemical composition of the porous aluminium oxide films is largely aluminium oxide with anionic species, such as phosphate or sulphate, incorporated from the electrolyte solution used in the anodising process. Figure 2 shows a scanning electron micrograph image of a typical film structure produced by anodising aluminium in sulphuric acid, where the pore diameter is ~80 nm.

Anodised aluminium film structures are already produced commercially by batch processing in, for example, the aerospace and window frame markets and also by continuous processing of aluminium coils in packaging and architectural sheet applications (see schematic in Figure 3). In this schematic, the entry and exit rolls act as guides to the coil feeding through the system, with a series of graphite electrodes applying appropriate voltage and current...
regimes, and spray rinse bars located at the ends of each section. Clearly, the ability to continuously anodise aluminium coils reflects a somewhat unrecognised opportunity to process large areas for anodic templates.

Modification and control of anodic film structures

The parameters which control the anodic film structure are shown schematically in Figure 4. These are essentially the anodising voltage employed, the charge passed during anodising, the degree of chemical dissolution occurring in the chosen electrolyte (oxide film dissolution and anodic film growth are competing processes) and the electrolyte chemistry itself. Whilst a wide range of electrolytes are employed, phosphoric, sulphuric and oxalic acids (or, in many instances, a combination of several of these) are the major electrolytes.

In some of the more technically demanding product applications, such as optoelectronic devices, a more long-range ordering of the anodic film oxide is required and this can, to some degree, be achieved by a two-stage anodising process. In such situations, a second anodising treatment is carried out after removal of the first anodic film in a chromate/phosphoric acid stripping solution. Figure 5 shows a scanning electron micrograph image of a sulphuric acid film structure achieved after two-stage processing; this latter image shows increased pore ordering (cf. Figure 2).

General applications

A wide and, perhaps surprisingly, varied range of the scientific literature has, over the last decade or so, described potential opportunities and applications for anodic film replication technology. These have included, for example, optoelectronic and magnetic (storage) nanowire and nanotube materials, solar and catalyst support devices, small biosensor concept devices, carbon nanofibres or nanorods, MoO3 nanorods as an improved cathode material for rechargeable lithium batteries, and multigram synthesis of copper nanowires. Such material or device fabrication is achieved through species deposition in the porous template using conventional techniques such as electrodeposition or chemical vapour deposition into the pores. Figure 6 schematically repre-
sent the materials’ incorporation into the porous oxide film and identifies potential applications in electronics, fuel cells, hydrogen storage and field effect transistors. In addition to these somewhat “hard technology” applications, the potential for replicating hydroxyapatite in the film structure has been demonstrated in the literature, raising the prospect of generating synthetic bone material for biomedical or orthopaedic devices.

Such examples clearly demonstrate an area of significant technological and scientific interest with the prospect for fuller commercialisation.

**Polymer replication for pressure sensitive adhesives**

The requirements in many of the more technologically demanding applications, such as electronic arrays, is for longer-range pore ordering and this can be a perceived limitation to fuller commercialisation of the anodic replication technology. With this aspect in mind Innoval Technology has been directing its development activities towards high value product opportunities where longer range ordering is possibly not necessary for product performance. One such application is in the pressure sensitive adhesive (PSA) market which has a global value of $20 billion in 2006 and a predicted annual growth rate of 6.5%; accessing even a fraction of this market with anodic film replication technology would represent a significant market opportunity.

Manufacturers of PSAs recognise the ability of the Gecko to adhere to a wide range of surfaces from the molecularly smooth to masonry. Whilst PSAs are normally chemically tailored to allow an object to be attached to a particular surface, more often than not the bond fails after relatively short periods of time due to contamination. In the case of the Gecko, nature demonstrates a universal type of adhesive is possible that can be placed and replaced on any surface without loss of bond strength. A self-cleaning mechanism that expels contamination from the bonding area is thought to be in operation and this too could lead to a range of new adhesive application opportunities.

In an attempt to simulate the Gecko feet structure porous anodic film structures, either adhering to the substrate or free-standing, have been used as templates for the fabrication of a wide range of inorganic or organic, micro and nanostructures. Structures similar to the setae (hairs) on Gecko feet that enable them to adhere to surfaces can be replicated using anodic films (see Figure 7) and this could lead to developments in the fabrication of a new generation of adhesive tape materials. Figure 7 compares images of Gecko feet setae (left image) with an image of polymer nanofibres (~0.2µm diameter) produced by Innoval using anodised aluminium as a template material.

Other replicates of the Gecko feet structure have been made using several polymer materials by casting them into 60 µm thick anodic films with 0.2 µm pore diameters, and the anodic oxide film removed leaving a polymeric replicate. This is exemplified in Figure 8 where a high density fibrous structure with a 300:1 aspect ratio has been produced using both polystyrene and neoprene. In addition, with appropriate polymer formulation or polymer surface modification, further surface functional characteristics can be introduced. Materials such as this (although possibly...
with much lower aspect ratios) have potential in adhesive applications where the structure simulates that of Gecko setae. Critical to this effort is the fact that long-range pore ordering, a prerequisite for some of the more technically demanding applications, is not a requirement for adhesive product applications. Equally important is the fact that this technology has the capability to produce fibres or materials with aspect ratios of 300:1, an aspect ratio not so readily achievable by other replication techniques and one which can be tailored to product requirements by employing different anodic film thicknesses and morphologies. Innoval Technology and Manchester University have been collaborating in the development of tailored anodic films, targeted towards different market and product sectors. In the case of polymer replication for adhesive applications, using non-ordered (but readily tailored in terms of pore dimensions) anodising technologies, there is significant market potential in a number of sectors, including both healthcare and general engineering applications.

A further advantage of anodic film templating over alternative replication technologies is the processing potential for large-area template manufacture. As discussed previously, the electrolytic processing of aluminium can be a continuous, relatively high speed process applicable to large diameter (>1 m) aluminium coils. No other replication-based technology is as advanced in its capabilities to produce such large volume template material.

**Summary**

Electrolytic processing of aluminium potentially offers a lower cost alternative to competing replication technologies (e.g. vacuum-based lithography) with the additional prospect for large area manufacture. Since aluminium anodising is an already existing manufacturing technology, with well-known capabilities for large-area batch and continuous manufacture, such a potential represents a significant opportunity for transferring products based on anodic film nano-replication from the laboratory to the industrial scale.

It has been demonstrated that replication of different polymers is achievable using anodic films, and these have potential applications in large scale adhesive tape manufacture. The global value of the pressure sensitive adhesive market is multi-billion and, as such, could represent a significant product opportunity for anodic film replication technology.

Innoval Technology and Manchester University have been collaborating on the development of tailored anodic film structures from aluminium, targeted towards different, high value, market and product sectors.

**Biographies**

Colin Butler and Eoghan McAlpine are Material Consultants with Innoval Technology in Banbury, UK. Colin has a PhD in polymer chemistry and Eoghan has a PhD in physical chemistry; each has over 25 years industrial R&D experience and have spent over a decade working on surface engineering and coating of aluminium substrates.

Innoval Technology is a technology consultancy providing advanced materials and process engineering expertise, primarily within light metal applications, and is actively collaborating in a number of innovative material and process technology developments.

George Thompson is the Head of the Corrosion and Protection Centre and Professor of Corrosion Science and Engineering at the University of Manchester, UK. His research interests include the surface treatment and modification of aluminium surfaces and he has published extensively in the field of aluminium anodising, metal surface treatments and corrosion science.