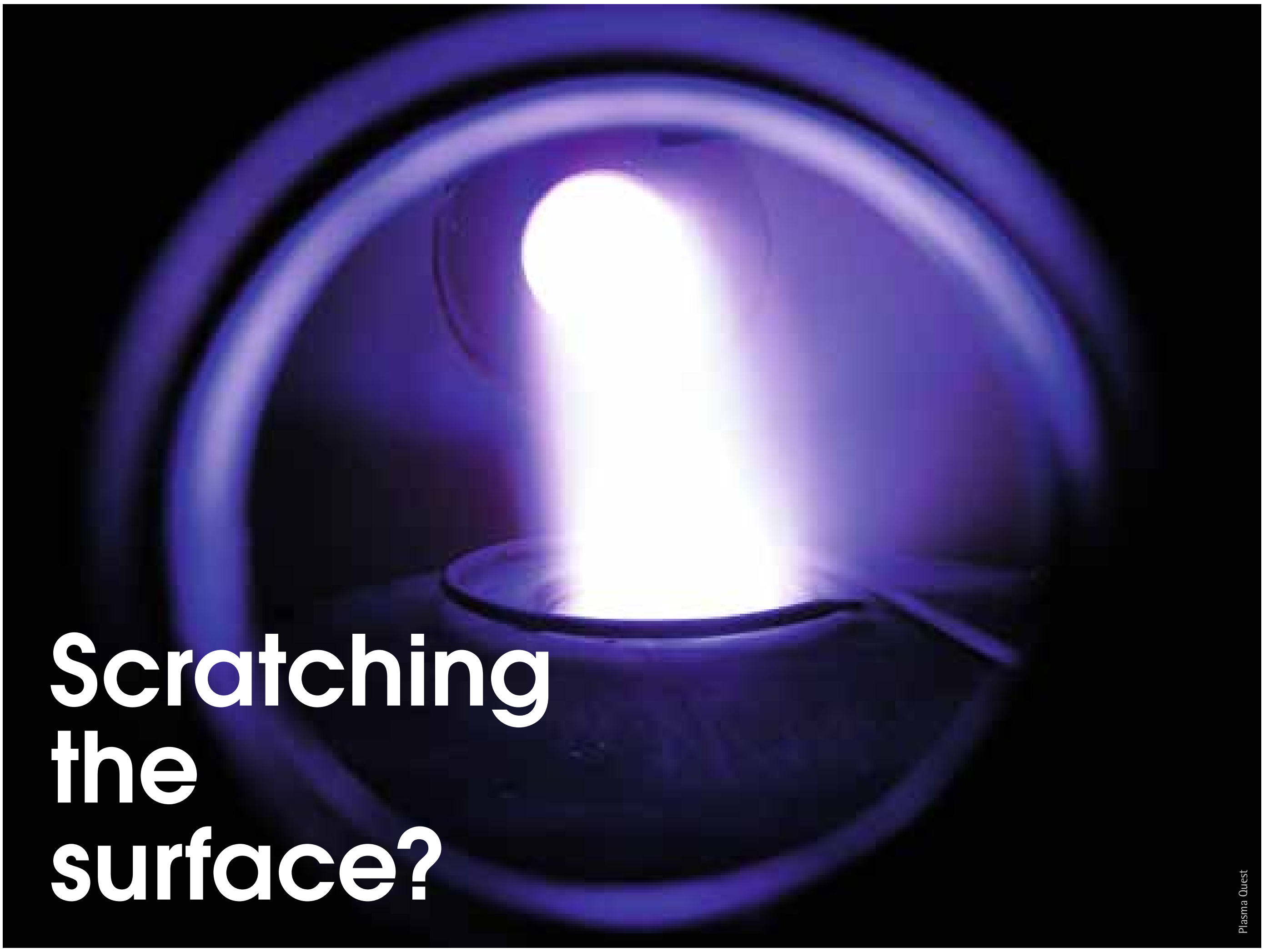


Scratching the surface?

Plasma Quest

Dr Martin Kemp looks at the ongoing developments in nano-enhanced surfaces.

Every object in our day-to-day lives has surfaces, both internal and external, and each has a function. The surface is the interface between the object and the surrounding environment, in its broadest sense, and its properties can be crucial to the overall component performance. Surface functionality or properties include mechanical, physical, aesthetics and chemical. In the 1990s, there was a drive to embody two or more functions in one surface, prompting the term "smart" coatings.

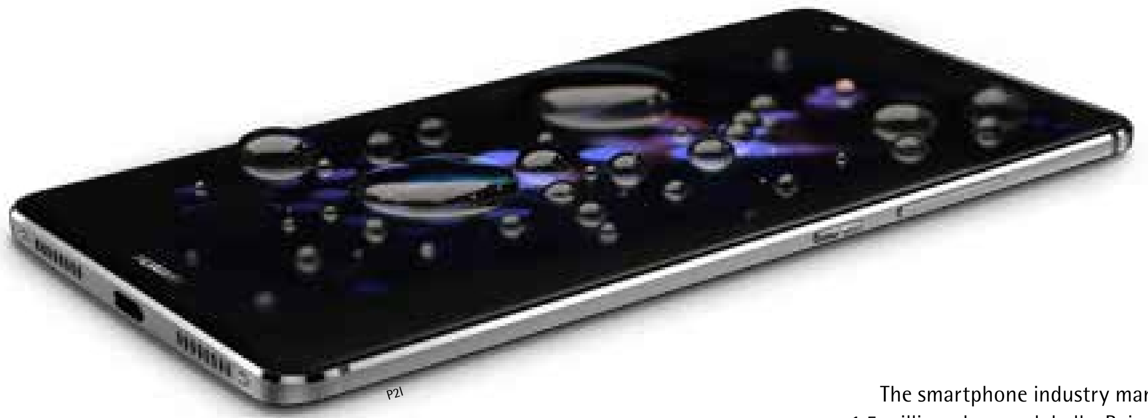
Nano-enhanced surfaces comprise of a nano thickness (less than 100nm) or nano-structured coating. Various processes are used based around physical plasma, chemical sputtering or wet-chemistry. One challenge has been developing nano-enabled surfaces for scale-up commercialisation and several companies have been working on developing specific applications for manufacturing these surfaces.

Plasma techniques

Man-made plasmas have proven to be a versatile route to manufacturing coatings, and a multitude of equipment variations have been developed. Plasma is often described as the fourth fundamental state of matter, comprising gas atoms, which either gain or lose electrons, becoming ionised. In a plasma, charged particles (with near equal amounts of ions and unbound electrons) and neutral atoms are free to move with overall charge neutrality. An example of a natural plasma is the Northern Lights phenomenon, where charged particles from the sun are captured by Earth's magnetic field, causing light emission by excitation/ionisation of atmospheric gases. Commercial processes based on physical vapour deposition (PVD) exploit plasma and are used in electronic, optics, architecture, food packaging and decorative coatings.

Water resistance for smartphones has made a major step forward in the past five years. Nanotechnology development company P2i, UK, has been involved in developing a plasma-enabled process that coats substrates with a water-repellent polymer layer several nanometres thick. The technology was initially designed for fabrics to protect soldiers from toxic hazards. The process uses a vacuum chamber in which a radio-frequency (RF) plasma is generated, creating free-radical sites on the substrate. A gas-phase monomer is then introduced and pulsed RF plasma produces polymerisation, converting the monomer into a polymeric layer on the surface of the item to be coated.

The initial market for P2i was dirt and moisture protection for sports footwear, with the P2i equipment installed directly into the production line. However, the process proved too expensive for this application, so attention turned to splash proofing hearing aids. P2i secured 60% of the global market, producing 14 million devices per year, and, as Stephen Coulson, Technical Director, explained, 'This caught the attention of the burgeoning mobile phone industry.'



P2i

Hardide Coatings

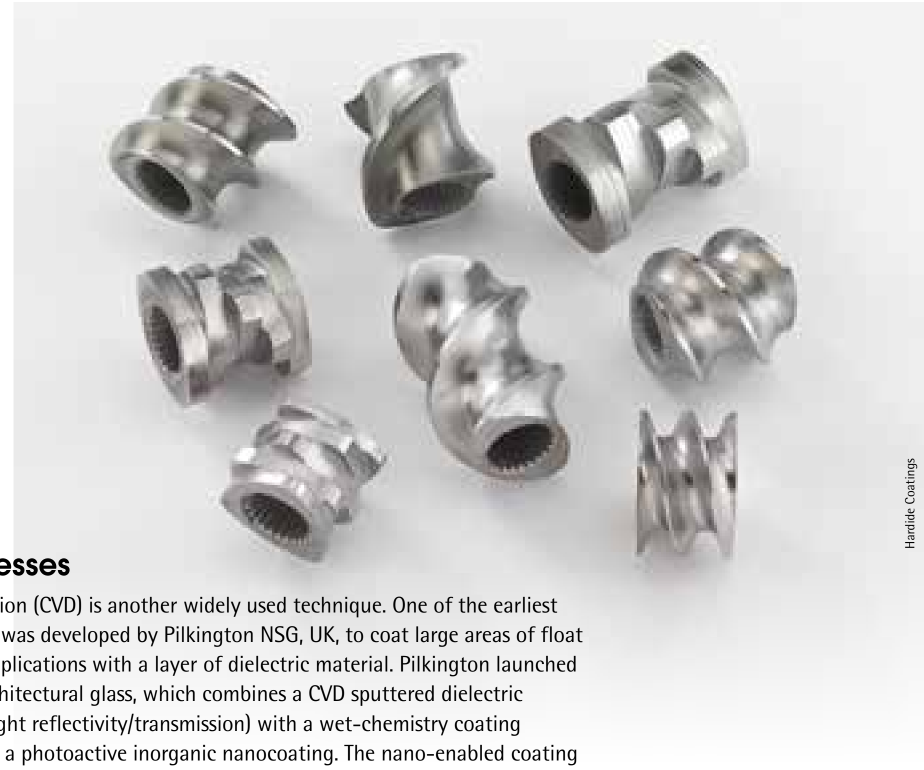
NikaWorks and RSL Steeper

The smartphone industry manufactures around 1.5 million phones globally. Being an expensive and water-sensitive electronic device, water ingress from rain, sweat and high humidity presents hazards, and considerable financial liability to manufacturers. Coulson notes that 4.5% of all returns are because of liquid damage, and a further 18% of failures caused by liquids are not reported, adding up to a financial liability of around £1.5bln per annum. Coulson predicts that future applications will emerge out of the Internet of Things (IoT). 'These new 5G based networks will depend upon a vast number of distributed sensors and devices, which will all need to be protected from the environment.'

Elsewhere, thin film deposition technology company, Plasma Quest Ltd (PQL), UK, has developed a different PVD technique using high-density magnetised plasma denoted high target utilisation sputtering (HiTUS).The technique comprises a remotely generated plasma, which is 'steered' onto the material to be sputtered, and deposits customised thin films of metals, oxides and dielectric materials onto a range of substrates including plastics. A negative bias is then applied to the target, which is deposited as a thin film on the surface to then be coated. The substrate and coating remain at a low temperature, which minimises film stresses when applied to plastic substrates.

A mainstay of PQL's coatings has been exploring novel transparent conducting oxides (TCOs), including indium-free compositions for plastic electronics, solar cells and infrared mirrors. One application is improving laser mirrors. The durable coating developed allows high laser power to be used without mirror degradation. Another application is in automotive sensors – vital for modern control systems. PQL has developed a coating exhibiting giant magnetic resistance (GMR) used for components including shaft rotation sensors, and wireless accelerator pedals. Professor Mike Thwaites, CEO of PQL, explained, 'An exciting future growth area is thin film coating for large-area, low-temperature roll-to-roll plastic electronics.'

PVD is an active area for new developments, and specialist companies such as NikaWorks Ltd, UK, have been developing and applying coatings for medical applications including surgical instruments for protecting the electrodes in contact with the human body required for operation of a bionic hand prosthetic. As Dr Alistair Kean, CEO of NikaWorks, stated, 'In a PVD process it is possible to add energy to the evaporated species by means of ionisation and electrostatics or by ion or plasma assist. In this way, it is possible to form extremely adherent coatings by essentially "merging" the materials'.



Hardide Coatings

Chemical processes

Chemical vapour deposition (CVD) is another widely used technique. One of the earliest commercial applications was developed by Pilkington NSG, UK, to coat large areas of float glass for architectural applications with a layer of dielectric material. Pilkington launched a novel self-cleaning architectural glass, which combines a CVD sputtered dielectric coating (for control of light reflectivity/transmission) with a wet-chemistry coating technique for depositing a photoactive inorganic nanocoating. The nano-enabled coating is activated by sunlight to degrade organic debris and as it is a hydrophilic coating, facilitates rain spreading over the glass surface and washing away the debris.

In contrast, CVD coatings are finding use in heavy-duty engineering. Hardide Coatings, UK, has developed a novel low-temperature, low-pressure CVD process in which the coating crystallises atom-by-atom from the gas phase to form a nano-structured coating. The coatings comprise tungsten carbide nanoparticles dispersed in a metal tungsten matrix. The resultant nanostructure has enhanced hardness, toughness and ductility and additional performance benefits including resistance to abrasion, erosion, corrosion and anti-galling under high loads without lubrication and protection of mating components such as seals and bearings. Typical substrates are stainless steel, inconel, copper, and nickel-copper alloys such as monel. Compared with line-of-sight coating methods such as thermal spray, PVD coatings or electroplating, the CVD process produces a uniform conformal coating, enabling the coating of components with complex geometries such as extrusion dies, ball valves or pump impellors.

An important environmental driver for new coatings is the replacement of hexavalent chrome plating. The aerospace industry will be restricted in the use of such coatings in 2017 by REACH legislation, and this has stimulated aircraft and component manufacturers who have traditionally used hard chrome to seek alternatives. Speaking about the key markets for Hardide Coating, Dr Yuri Zhuk, Technical Director of Hardide Coatings, explains, 'The largest application area has traditionally been in the offshore oil and gas drilling industry, where longer tool life can help reduce downtime, which can cost operators US$1m per day. In the last few years, we have developed coatings for new industry sectors including aerospace, with the Hardide coating securing technical qualification from Airbus as an alternative to hard chrome plating.'

An unconventional application of the coating is tools for cutting and drilling, rock, glass, stone, as well as composites and non-ferrous metals. Conventionally, diamond-tipped tools are used, but polycrystalline diamonds are very difficult to attach to metal tool bodies as they exhibit poor wetting properties to the molten metallic phase. The Hardide tungsten carbide coating adheres to the diamond and has good wetting by the molten metals used in brazing. Maintaining drill dimensions and cutting performance is important when drilling durable materials, such as carbon fibre composites for aerospace – a critical application for damage-free holes – essential to ensure structural stability.

Scale-up is an important factor for multi-component manufacture, and the Hardide coating is applied in batch process coating to produce a large number of smaller components. Asked for views about the overall impact that the coating could have, Zhuk said, 'According to a recent report by the Innovate UK – SEAC SIG working group, the value of coatings applied in the UK advanced manufacturing supply chain is around £11bln per year, affecting products worth more than £140bln. We are enhancing UK competitiveness in high wear and value manufacturing industries by offering high performance and increased cost effectiveness'. Nano-enhanced surfaces and coatings are now mainstream, and the few examples here have only just scratched the surface of a wide and diverse industry enabling future manufacturing.

Above: Hardide can coat internal surfaces and complex geometries.

First page top: Plasma Quest's remote high-density plasma during the HiTUS deposition process to produce high-quality thin films.

Opposite top: P2i's patented pulsed plasma deposition process provides the highest levels of liquid repellency for the mobile phone industry.

Opposite middle: Components being loaded into Hardide coating reactor.

Opposite bottom: Biocompatible PVD coated electrodes for a bionic hand product.

Dr Martin Kemp CEng FIMMM is the Chair of IOM3 Nanomaterials Committee and Founder of Xcience Ltd.

The IOM3 Nanomaterials committee will be holding a one-day event on nano-enhanced surface technologies on 25 May, register online at **bit.ly/2jd3Jcb**