# Shot Peening: A Powerful Surface Coating Tool for Biomedical Implants

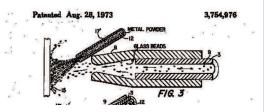
hot peening is widely used in the automotive and aerospace industries to reduce fatigue failure. However, shot peening and grit blasting have also been adapted to embed or coat materials onto metal surfaces and offer benefits to the biotechnology field. Three classes of modified shot peening and grit blasting techniques have been employed to this end:

- abrasive blasting or shot-peening processes utilizing a single type of solid particle comprised of a single phase
- abrasive blasting or shot-peening processes utilizing a single type of solid particle comprised of multiple phases
- abrasive blasting or shot-peening processes utilizing multiple types of solid particles, the solid particles themselves comprised of a single phase

Examples of the first class of coating technique are found in patents filed by Kuo<sup>1</sup> and by Arola and McCain<sup>2</sup>. In such processes, the single phase solid particle is carried to the substrate surface at high velocity in a gas or liquid stream. On impact, shattered pieces of the particulate embed in the metal surface. Such processes have been used to embed ceramic materials as the particles must have the appropriate properties of brittleness, hardness, size and mass to embed in the surface when projected at velocities achievable in ordinary blasting or shot peening equipment. The mechanics of the process restrict it to the embedment of particles at random in the surface and a coherent coating on the surface cannot be achieved by this means.

The multiple-phase solid particles in the second class of coating technique typically comprise a hard and soft phase, the harder phase embedding the softer phase into the metal surface. In the Rocatek<sup>™</sup> bonding system developed by 3M, pre-roughened metal substrates are bombarded with composite particles of a hard core of alumina and a thin outer laminar layer of softer amorphous silica. On impact, the interface between the outer silica and the core alumina is broken and the energy dissipated fuses the silica to the surface of the substrate. Other examples are to be found in the work of Müller and Berger<sup>3</sup> and Bru-Maginez et al.<sup>4</sup>

The third class of coating technique, known in its earliest incarnation as peen plating, was developed in the 1970s and 1980s by a team of scientists working for the National Aeronautics and Space Administration (NASA) on the thermal, wear and corrosion properties of metals used in the aerospace industry. The earliest peenplating patent by Babecki and Haehner<sup>5</sup> describes a process where a stream of fine aluminum and/or copper powder (the coating) is impacted onto a metal surface by the simultaneous peening action of a stream of glass bead shot. Subsequently the peen plating process was optimised and extended to coating with other fine metallic powders<sup>6</sup> and non-metals<sup>7</sup>. Fig. 1 is an illustration of one configuration of the peen plating process taken from Babecki and Haehner's patent.



#### Fig. 1: An illustration from the peen plating patent of Babecki and Haehner

The peen plating process was further developed for coating metallic substrates with solid-state lubricants such as molybdenum disulphide. SURFGUARD was successfully commercialised by Techniblast Co. under licence from NASA<sup>®</sup> and the equipment used in the SURFGUARD process was patented by R. Spears<sup>9</sup>. Subsequent to the invention of the peen plating process, many variants on the theme of using the action of particle collisions to adhere materials to the surface of metals have been developed for a wide range of applications including the addition of biocompatible ceramics to the surface of biomedical implants<sup>10, 11</sup>.

It has been recently established that high temperatures are induced in substrates during collision processes such as shot peening<sup>12-14</sup>. It is estimated that between 70% and 90% of the incident kinetic energy transferred to the substrate is converted to heat in the uppermost layers. In light of this, it is not surprising that whether used in the aerospace, biomedical or other industrial sectors, previous shot peening-based coating processes, such as developed by NASA, have been limited to the coating of metal substrates with fine ceramic or metallic powders primarily because these coating materials can withstand the heat generated during the collisions accompanying shot peening and because these materials are readily available in fine particulate form.

#### by Dr. Donncha Haverty and Dr. Brendan Kennedy of HKPB Scientific Ltd., Ireland

Dr. Haverty and Dr. Kennedy are graduates of the University of Limerick (UL), Ireland. They have established a spin-out biotechnology company from UL focused on solving the urgent bio-active coatings problems encountered in the medical devices industry today. Their patent-pending technology is a modified shot peening-based technology called Temperature Moderated - Collision Mediated Coating (TM -CMC) that allows for the coating of medical devices with thermally sensitive therapeutic agents in an one-step process.

Temperature Moderated – Collision Mediated Coating  $(TM - CMC)^{15}$  was developed to circumvent the limitations of previous coating techniques and enable the coating of substrates with thermally sensitive materials, such as therapeutic agents or polymers. The process involves atomising a liquid-based precursor coating composition to form an aerosol which is directed to the surface of the substrate in conjunction with a stream of shot particles. The collision energy released by the impacting shot mediates the transformation of the precursor composition into a well-adhered coating in a one-step process without the requirement for complex curing agents or subsequent heat treatments.

The results of initial proof of concept experiments are shown below. Fig. 2 shows the antibiotic release assay with bacterial kill zones around titanium stubs coated with hydroxyapatite and the antibiotic gentamicin using the TM – CMC process (the different sizes of the kill zones are the result of differing concentrations of gentamicin in the coatings). The stubs were ultrasonically cleaned after coating and incubated for 36 hours at 37°C (98.6°F) in bacterial cultures of *E. Coli*. The kill zones, where no bacteria have grown, are the result of gentamicin eluting from the coating on the titanium stub into the broth on which the bacteria grow. The antibiotic remains active through the process in all three titanium stubs.



Fig. 2: Antibiotic Release Assay for three titanium stubs coated with hydroxyapatite and gentamicin using the TM – CMC process.

An example of a polymer coating applied by TM - CMC is in Fig. 3 where a Focused Ion Beam Image of a milled section of a Teflon coating on a titanium stub is shown. The precursor composition was a dispersion of 200 nm Teflon particles in n-hexane solvent and it is clear that the morphology of the starting precursor composition is manifest in the adhered layer wherein the coating being formed by the compaction of the liquid-dispersed particles of nanometer dimensions contains pores of similar size.

This early work demonstrated that the range of materials that can be coated by TM-CMC is not restricted to inorganic solids but, under appropriate operating conditions, the technique may be used to incorporate thermally sensitive materials into coatings. We believe that this novel, patent-pending coating technique has the capacity to solve many of the urgent problems facing bioactive coatings in the medical device arena such as the problem of late stent thrombosis encountered with the Drug Eluting Stent.

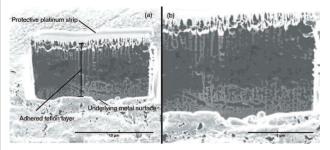


Fig. 3: A Focused Ion Beam of a titanium stub coated with Teflon

Mechanistically, while the energy released on collision of the shot with the surface is necessary to transform the precursor composition into a coating, unchecked the consequential temperature rise that would result would be detrimental to the inclusion of thermally sensitive components. The key to incorporating thermally sensitive components is moderating this heat. This is achieved through the liquid element of the aerosol, which absorbs part of the heat generated and protects the thermally sensitive components, and where necessary, the underlying substrate. Precise control of the atomisation and composition of the liquid-based precursor appears critical to the process: insufficient liquid and the temperature moderating effect is absent while excessive liquid prevents the formation of a coating.

Using a liquid medium also extends the range of materials that can be coated beyond particles. Many potentially advantageous coating compositions are not available in particulate form. For example, nano-particles are generally supplied as colloidal suspensions to prevent agglomeration and/or to protect chemical functionality with which they may be augmented. In addition, the process may readily extend to the precursor gels, sols and resins of a wide range of polymers and ceramics without the requirement for complex chemical coupling or curing treatments, circumventing the biocompatibility problems that such components present in coating methodologies currently employed in the biomedical sector.

Furthermore, TM – CMC is easily implemented in a manufacturing environment, combining two widely used and readily automated equipment platforms, atomisation and shot peening, in a new way. The company's current efforts are directed towards exercising the necessary control over the process to ensure reproducibility and quality.

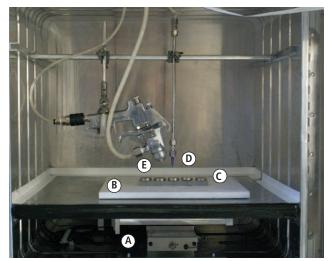


Fig. 4: The TM – CMC automated test rig

Fig. 4 shows an automated rig developed by HKPB Scientific for generating reproducible samples for physical, chemical and biological testing. The rig consists of an upper and lower chamber that are isolated from each other. An XY positioning table (A) located in the lower chamber is used to accurately move and position the sample platform (B) and the test samples (C) below the shot peening nozzle (D) and the two fluid atomiser (E). The shot peening nozzle and the two fluid atomiser are positioned so that the streams of shot and atomised coating precursor are directed to the same spot on the samples so that a coating is formed according to the mechanisms described earlier. HKPB Scientific uses aluminum oxide and glass bead media purchased from a manufacturer of microabrasive blasters for the medical device industry.

Dr. Haverty and Dr. Kennedy anticipate that the ability to control the density and energy with which the primary collision particles (shot) strike the surface in conjunction with the choice of solvent provides enormous scope for TM-CMC as a coating process. HKPB Scientific is targeting three key applications:

#### Hard Tissue Implants

TM – CMC has the potential to solve the two major problems encountered in the arena of hard-tissue implants: aseptic implant loosening and infection.

#### **Drug Eluting Stents**

TM – CMC has the potential to offer improvements in the area of cardiovascular drug delivery by reducing the incidence of post-operative complications and improving the stent's drug delivery.

#### **Pacemakers and Defibrillators**

Based on Centre for Disease Control (CDC) research (Klevens et al., 2007), Hospital Acquired Infections (HAI) are responsible for 5% of surgical failures of pacemakers and defibrillators. Pacemakers have been identified as a medical device that would benefit from antimicrobial coatings but currently no effective methodology exists to coat pacemakers with suitable anti-microbial formulations. TM - CMC allows for the low temperature deposition of coatings comprising a range of biocompatible materials, which may be augmented with antibiotics.

Further details on the TM – CMC process can be accessed on the HKPB Scientific website at www.hkpbscientific.com. HKPB Scientific is actively seeking partners with an expertise in automated shot peening, atomisation and related CNC and encourages those who are interested to contact us through our website.

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