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(54) ABRASIVE BLAST MODIFICATION OF SURFACES

(57) A metal surface treatment method wherein the surface (10) is simultaneously bombarded with a mixture of abrasive particles (4) and dopant particles (6) which are delivered at a velocity in the range of 50-250 m/sec, and thereby depositing the dopant material on the surface, the dopant being a polymer and the abrasive having an average particle size in the range of 5-5000 microns. Also provided is an article (8) having a surface treated by such a method.

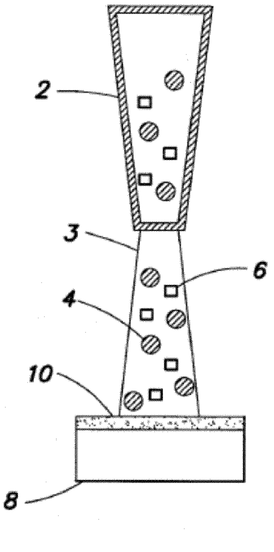

Figure 2a

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Description

Field of the Invention

[0001] The present invention relates to surface treatment techniques in the field of materials science.

Background to the Invention

[0002] Metal surface finish is often provided using particle bombardment. This can vary from material removal using abrasive blasting through to material deposition using cold spraying. The difference in these approaches rests in the energy of the processes. Despite its name, the cold spray process actually uses elevated temperatures. The gas used to carry the particles is heated to a temperature of several hundred degrees, typically between 200°C and 1000°C, before it is mixed with the bombardment particles. This increases the gas velocity without increasing the line pressure feeding the gas. Typically cold spray processes operate at elevated temperatures but below the melting point of the metallic bombardment particles that are employed. In addition to the thermal energy provided by the heated gas, the kinetic energy of the bombarding particles is also higher in cold spray systems as the particles travel at significantly higher velocities than in abrasive blasting. The particles are typically accelerated to supersonic speeds (greater than 342 m/sec). At high velocities, greater than 300 m/sec, the energy imparted by the impact of the particle against the surface can be sufficient to cause both the metal surface and the bombarding metal particle to deform and the resultant interaction causes the particle to spread out and coat the surface. The minimum velocity required to achieve this coating deposition is referred to as the 'critical velocity' in cold spray technology. Due to the requirement for the bombarding particle to deform upon impact, there has been limited applicability of this technology to the deposition of non-metallic materials. At values below the critical velocity, very little impregnation of the surface occurs and the bombarding particles typically bounce off the surface. The widely quoted minimum critical velocity for a wide range of materials is 400 m/sec, as outlined in Grigoriev et al. (Surf. Coat. Technol., 268 (2015), pg 77-84) and as shown in the present Figure 1, which is taken from that publication. This value can vary depending upon the bombarding particles and the properties of the substrate surface.

[0003] In most metallic materials an oxide layer forms at the surface, which will be harder than the bulk metal or alloy. Metal surfaces (especially those of titanium and titanium derived alloy) are naturally contaminated in air by a variety of contaminants. The detailed physical and chemical properties of any metal surface depend on the conditions under which they are formed. The inherent reactivity of the metal can also attract various environmental chemicals/contaminants that oxidize on the surface. For example, titanium is a highly reactive metal, which is readily oxidized by several different media. This results in titanium, and most other metals, always being covered in an oxide layer. This oxide layer is chemically stable and much harder than the bulk metal underneath. As the metal oxide is typically much harder and less reactive than the metal, the ability of the bombarding particles to bond to the substrate is often limited by the properties of the oxide and not by the properties of the underlying metal.

[0004] This is also true of cold spray technologies, which are also limited by the properties of the surface that can be treated. In order for the cold spray coating to adhere, the substrate surface must be cleaned and roughened. This is often accomplished by abrasively blasting the surface before cold spraying. In some instances, cold spray coatings have been undertaken which also incorporate some abrasive particles alongside the metal dopant, but these have all been deposited at high velocities and at elevated temperatures beyond the range of abrasive blasting. Experimentally, it has been found that the presence of the ceramic particles acts to increase the deposition rate of the metal. In addition, the presence of the ceramic may enhance the wear resistance of the deposit.

[0005] Most surface bombardment processes are not focussed on material deposition, but rather on surface roughness and stress. If round particles are used to bombard the surface and the velocity is low enough, at subsonic speeds that are below the critical velocity, then the surface is merely deformed and dimpled by the bombardment. This is referred to as shot peening and it is routinely used to control surface stress by applying compressive stress to the surface, and this process leaves a characteristic dimpled surface appearance.

[0006] If particles with an angular or irregular morphology are used to bombard the surface at values below the critical velocity, then the edges and corners of the bombarding particles can cut up and erode material from the substrate metal. This results in abrasion of the surface, and abrasive blasting is widely used to clean and roughen metal surfaces. For optimum abrasive effects, the abrasive particles are chosen to have a Mohs hardness of at least 5, though harder particles are preferred as the abrasion increases with hardness.

[0007] During the abrasive blasting process, it has been observed that some particles of abrasive are left impregnated in the substrate. For many applications, this is considered a detrimental effect and further etching or cleaning steps are required to remove the contamination. However, there are applications where the contamination arising from abrasive blasting has been postulated to be beneficial. US 4,194,929 describes a process wherein a stainless steel surface is blasted with iron or steel abrasive. As ferrous particles are embedded in the corrosion resistant steel surface, this causes a passivating coating to form in a conventional phosphating solution. In US 7,377,943, Müller et al. describe a process for improving the bioactivity of a metal surface by blasting the surface with a powder wherein each particle comprises a vitreous crystalline material made from a combination of CaO, P_2O_5, ZrO_2 and fluoride. The resultant particles are embedded in the surface to improve the biocompatibility of the metal surface. These methods all involve bombarding the surface with a single type of particle and feature a combination of abrasion and impregnation.

[0008] In a further development of this, Ishikawa et al. (J. Biomed. Mat. Res. (Appl. Biomat.), vol. 38, pg. 129-134, 1997) reported on the blasting of titanium with a hydroxyapatite powder using conventional abrasive blasting equipment. They observed that the powder built up on the metal surface without any evidence of substrate abrasion when examined using electron microscopy. They attributed this coating formation to the reactivity of the hydroxyapatite material which resulted in a form of particle sintering and to some adhesion to the surface. Although stable to ultrasonic washing, the coating was removed by scratching with a steel blade, indicating only moderate coating adhesion was achieved. This suggests minimal bonding of the bombarding particles to the metal and microscopy seems to confirm this, with no evidence of metal abrasion evident. This may be due to the hard passive oxide layer that is present on titanium. The soft hydroxyapatite particles would therefore not be expected to rupture and abrade the metal oxide.

[0009] Others have sought to deposit materials on the surface of a metal using a combination of two sets of particles which are dissimilar. US 3,754,976 describes a process for metal plating. While cold spray uses high velocity bombardment to adhere a metal to a surface, this patent disclosed a process for metal plating in which a mixture of metallic powder and small shot peening particles are sprayed against a surface at a velocity sufficient to impact and bond the metallic powder onto the surface. The peening particles effectively deform and plate the metal particles onto the surface without any significant uptake of peening particles in the coating. This technique was later expanded to include additional materials that could be deposited. US 4,552,784 describes a process for depositing rapidly solidified metal powder using this technique. US 4,753,094 claims a process wherein a combination of molybdenum disulphide and round metal shot was blasted at a surface to deposit a layer of molybdenum disulphide. US 2006/0089270 claims a process wherein shot peening particles are mixed with a primary lubricant such as molybdenum disulphide and a polymeric lubricant such as polytetrafluoroethylene (PTFE) and blasted at a surface to deposit a mixture of the two lubricants on the surface. In all of these dual blasting methods, the inventors chose to use shot peening particles to bombard the surface alongside the coating material as the spherical shot peen particles would not abrade the coating as it deposited. Convention dictated that blasting with a combination of abrasive particles and a coating precursor would not produce a deposited coating as the abrasive would have been expected to remove any coating that formed.

[0010] In order to combine roughening of an abrasive blast process and a deposition process in a single step, others have looked at complex stratified particles in which an abrasive is covered with the coating forming material. The Rocatec™ system for the silicization of metallic and other surfaces uses individual particles having multiple components. This technology is used extensively in the dental arena. In this instance an alumina particle having an outer adherent layer of silica is propelled at a pre-roughened surface and upon impact the local heat generated in the vicinity of the impact causes the shattered silica outer layer to become fused to the surface through a process referred to as ceramicization. Similar strategies are outlined US 6468658 and US 6431958 in which abrasive particles are coated with a material and then blasted at a surface in order to embed the outer layer in the surface. In all of these cases, the abrasive is contained within an outer shell and therefore abrasion is limited and the surface is chemically modified. However these techniques all require the use of complex coated media which is expensive to produce, and this was deemed necessary as simply blasting with a simple mix of abrasive particles and coating material was not considered due to the expected removal of the coating by the abrasive action.

[0011] Despite this widespread belief, it was discovered by O'Donoghue et al. (EP 2061629 and US 8119183) that a combination of abrasives and coating materials could prove beneficial. Previous mixed media coatings had focussed on the use of round shot peen media that merely deposited the precursor powder as a laminate layer on top of the passive oxide that covered the metal. These laminate layers were prone to poor adhesion and could delaminate. By grit blasting the surface with a combination of abrasive and dopant, it was found that the abrasive removed the passive oxide layer and roughened the surface. With the hard passive oxide layer removed and a reactive layer of metal exposed, this facilitated impregnation of the dopant into the metal. This did not produce a laminate layer and ensured excellent adhesion of the dopant to the substrate, and this technique has been commercialised under the trade name CoBlast. Due to the tendency of metal dopants to deform and spread rather than shattering and embedding into the surface, the method is better suited to the deposition of non-metallic dopants.

[0012] While blasting a mixture of abrasive and dopants at a surface using the established CoBlast technique was effective at depositing materials into the substrate (and indeed there is no question that EP 2061629 (and related patents) discloses its invention in a manner sufficiently clear and complete for it to be carried out by a person skilled in the art) the optimum process parameters for CoBlast were not well understood. In particular, the critical particle delivery velocity required to impregnate the surface with a dopant was not well established, and sub-optimal coatings could therefore result.

[0013] There has therefore been a desire to improve the CoBlast technique through improved identification of process parameters, in particular in respect of the particle delivery velocity.

Summary of the Invention

[0014] According to a first aspect of the present invention there is provided a metal surface treatment method wherein the surface is simultaneously bombarded with a mixture of abrasive particles and dopant particles which are delivered at a velocity in the range of 50-250 m/sec (metres per second), and thereby depositing the dopant material on the surface.

[0015] For instance, the particles may be delivered at a velocity in the range of 100-200 m/sec, for example at a velocity in the range of 120-180 m/sec.

[0016] The method may be carried out at ambient temperature.

[0017] Preferably the abrasive particles have an irregular or angular morphology.

[0018] The dopant may be directly chemically bonded to the metal surface without any intermediate oxide layer. Alternatively, or in addition, the dopant particles may be agglomerated together on the metal surface.

[0019] Preferably the abrasive has a hardness greater than 6.0 on the Mohs scale. For example the abrasive may have a hardness of 8.0 or above on the Mohs scale.

[0020] Preferably the abrasive has a hardness at least 2 levels higher than that of the dopant on the Mohs scale. Particularly preferably the abrasive has a hardness at least 3 levels higher than that of the dopant on the Mohs scale.

[0021] In certain embodiments the dopant may be a polymer or other low density material (having a density of less than 2.5 g/cm^3) and the abrasive may have an average particle size in the range of 150-1500 microns (μm). For example, the abrasive may have an average particle size in the range of 250-1000 microns, such as in the range of 350-750 microns. As a further example, the abrasive may have an average particle size of greater than 300 microns.

[0022] In other embodiments the dopant may be a polymer (or alternatively may be a non-polymer), and the abrasive may have an average particle size in the range of 5-5000 microns, such as in the range of 5-1500 microns. For example, the dopant may be a polymer and the abrasive may have an average particle size in the range of 10-150 microns. Merely as two illustrative examples, we have achieved good deposition of polymer dopants using abrasive particles having an average particle size of 13 microns and, separately, using abrasive particles having an average particle size of 50 microns. The variation in abrasive size is typically associated with the desired texture required on the finished surface.

[0023] With the dopant being a polymer, the abrasive may constitute at least 60wt% of the mixture of abrasive and dopant particles. Preferably the abrasive constitutes at least 70wt% of the mixture of abrasive and dopant particles. More preferably the abrasive constitutes at least 80wt% of the mixture of abrasive and dopant particles.

[0024] In other embodiments the dopant may be a non-polymeric material and the abrasive may have an average particle size of less than 500 microns. For example, the abrasive may have an average particle size of less than 200 microns, or less than 150 microns. With the dopant being a non-polymeric material, the dopant may constitute at least 20wt% of the mixture of abrasive and dopant particles. Preferably the dopant constitutes at least 25wt% of the mixture of abrasive and dopant particles. More preferably the dopant constitutes at least 40wt% of the mixture of abrasive and dopant particles.

[0025] More generally, the dopant particles may have an average particle size in the range of 1-100 microns.

[0026] Typically less than 10 microns of dopant material are deposited on the surface.

[0027] At least some of the dopant particles may penetrate the metal surface and remain physically impregnated in the metal.

[0028] Depending on the application, one or more additional coatings may subsequently be applied on top of the deposited dopant material. For example, an additional coating may be applied through a bombardment technique selected from cold spray, peen plating or microblasting. Other ways of applying an additional coating are also possible, such as powder coating or painting.

[0029] According to a second aspect of the present invention there is provided an article having a surface treated by a method in accordance with the first aspect of the invention.

[0030] According to various embodiments of the first and second aspects of the invention, the surface that is treated may be at least a part of:

an implantable medical device;
a marine or land-based vehicle;
an aerospace vehicle, satellite, rocket or spacecraft;
an electronic device or component;
a mould; or
a pipe, tube or storage vessel.

[0031] Other applications are also possible, as those skilled in the art will appreciate.

Brief Description of the Drawings

[0032] Embodiments of the invention will now be described, by way of example only, and with reference to the drawings in which:

Figure 1 illustrates the classification of thermal spray processes in accordance with particle velocity and flame temperature (from Grigoriev et al.);
Figures 2a, 2b and 2c schematically illustrate a process for treating a metal substrate;
Figures 3a, 3b and 3c are schematic diagrams of

three different nozzle configurations to deliver abrasive particles and dopant particles to a surface;

Figure 4 shows optical micrographs of a 12 micron thick nickel layer electrolytically plated onto aluminium, (A) untreated and (B) following a CoBlast treatment to deposit calcium phosphate;

Figure 5 shows EDX analysis of the untreated nickel plate of Figure 4(A) and of the calcium phosphate surface of Figure 4(B) deposited onto the nickel plate (the calcium phosphate example being referred to as "Solar Black" in Figure 5); and

Figure 6 shows optical micrographs of a superelastic NiTi wire onto which polytetrafluoroethylene (PTFE) had been deposited (a) without the use of abrasive particles, (b) by a CoBlast treatment using <50 μm alumina abrasive particles, and (c) by a CoBlast treatment using <90 μm alumina abrasive particles, in each case before and after flexural testing of the wire.

Detailed Description of Preferred Embodiments

[0033] The present embodiments represent the best ways known to the applicants of putting the invention into practice. However, they are not the only ways in which this can be achieved.

Overview of CoBlast method

[0034] For the general details of the CoBlast method, the reader is initially referred to WO 2008/033867, which describes techniques for the substantially simultaneous deposition of first and second sets of particles. Naturally, as those skilled in the art will appreciate, the first and second sets of particles are different from one another. That is to say, the dopant species is different from the abrasive.

[0035] Embodiments of the CoBlast method are encompassed in but not limited to the schematic representation shown in Figures 2a, 2b and 2c.

[0036] Figure 2a schematically shows a fluid jet (nozzle) 2 that delivers a stream 3 comprising a set of abrasive particles 4 substantially simultaneously with a set of dopant particles 6. Particle sets 4 and 6 bombard a surface 10 of a metal substrate 8, to impregnate the surface of the metal substrate with the dopant.

[0037] In the schematic representation of Figures 2a, 2b and 2c, the surface 10 is a metal oxide layer. As a result of bombardment by the abrasive particles 4, the surface oxide layer is disrupted, and breaches in the oxide layer 10 result to expose a new surface 10a of substrate 8 (Figure 2b). In the case of a metal substrate, the newly exposed surface is a metal surface. As the particle stream 3 continues to impinge the substrate 8, the dopant particles 6 are integrated into the surface 10 of the substrate 8 (Figure 2c).

[0038] In some embodiments, the blasting equipment can be used in conjunction with controlled motion such as CNC (computer numerical control) or robotic control. Either the blast nozzle, the substrate or both may be manipulated so as to achieve the desired surface treatment. The blasting can be performed in an inert environment. The use of an inert atmosphere is typically required to manage explosion or flammability risks associated with dopant or substrate materials and is not a specific requirement in forming a coating.

[0039] In one embodiment, the dopant and abrasive particles are contained in the same reservoir and are delivered to a surface from the same jet (nozzle). In another embodiment, the dopant particles are contained in one reservoir and the abrasive particles are contained in a separate reservoir, and multiple nozzles deliver the dopant and abrasive particles. The multiple nozzles can take the form of a jet within a jet, i.e., the particles from each jet bombard the surface at the same incident angle. In another embodiment, the multiple nozzles are spatially separated so as to bombard the surface at different incident angles yet hit the same spot on the surface simultaneously.

[0040] Figures 3a, 3b and 3c are schematic diagrams of three different nozzle configurations to deliver the dopant and abrasive particles to a surface: single nozzle (Figure 3a); multiple nozzles with dopant and abrasive particles delivered from separate reservoirs where one nozzle is situated within another nozzle (Figure 3b); and multiple, separate nozzles with dopant and abrasive particles delivered from separate reservoirs (Figure 3c). More specifically, Figure 3a shows a single nozzle 20 for delivering a single stream 23 of abrasive particles 24 and dopant particles 26 to a substrate 28. Figure 3b shows that multiple nozzles with dopant and abrasive particles delivered from separate reservoirs can be used, with Figure 3b illustrating one nozzle 30 for delivering a stream 33 of abrasive particles 24 situated within another nozzle 40 for delivering a stream 43 of dopant particles 26, where streams 33 and 43 are coaxial. Multiple, separate nozzles with dopant and abrasive particles delivered from separate reservoirs can also be used, as indicated in Figure 3c, which shows nozzles 30 and 40, for delivering streams 33 and 43 of abrasive particles 24 and dopant particles 26, respectively.

[0041] The distance D between the nozzle(s) and the substrate surface can be in the range of 0.1 mm to 250 mm, such as a range of 0.1 mm to 130 mm, or a range of 5 mm to 50mm. The angle of the nozzle to the surface can range from 10 degrees to 90 degrees, such as a range of 30 degrees to 90 degrees, or a range of 70 to 90 degrees.

[0042] More than one type of dopant species can be used. It will readily be appreciated that where more than one type of dopant is used, the dopants may be delivered from a single nozzle, or each type may respectively be delivered from a separate nozzle.

[0043] More than one type or size of abrasive can be used. This may be undertaken to both assist in the deposition of dopant material and also to customise the surface topography and level of texturing during processing. It will readily be appreciated that where more than one type of abrasive is used, the abrasives may be delivered from a single nozzle, or each type may respectively be delivered from a separate nozzle.

Optimised CoBlast method

[0044] Although higher particle velocities are known to assist with deposition, these require increased gas pressures or temperature and this increases the cost of the process. Therefore, an optimised coating can result from premixing an angular abrasive with a particulate dopant, and delivering the powder mix to a metal substrate surface at a velocity of 50-250 m/sec, so as to remove the oxide layer from the surface, and simultaneously depositing less than 10 microns of dopant on the surface. At least a portion of the deposited materials penetrate the metal surface and remain impregnated within the metal. This process also results in direct chemical bonding of the dopant to the surface, without the presence of any intermediate oxide layer. In a preferred embodiment, the mixture of abrasive and dopant particles is delivered at a velocity of 100-200 m/sec to the surface. Optimally, the particles are delivered at a velocity of 120-180 m/sec. If the dopant particles are delivered at a different velocity than the abrasive particles, then it has been found that the velocity of the abrasive particles dominates the effect at the surface, and therefore it is the abrasive that has to be delivered at the correct velocity.

[0045] To achieve optimal impregnation of the dopant into the surface, an angular abrasive particle with a hardness greater than 6.0 on the Mohs scale is required. Using a harder abrasive can increase the deposition rate and an abrasive with a hardness of 8.0 or above is preferred. Using an abrasive such as this is sufficient to remove the oxide layer from a metal even at low velocity. In addition, the abrasive cleans the surface and ensures that no complex cleaning or roughening of the surface is needed prior to deposition. However, when mixed with a dopant delivered at a velocity of 100-200 m/sec, it has been found that the abrasive removes the oxide and also erodes some of the metal underneath. Due to the simultaneous abrasion and dopant delivery, several microns of dopant are deposited and this replaces the lost metal and metal oxide, and the cumulative effect is that the overall thickness of the substrate remains similar to that of the starting material. When using an angular or irregularly shaped abrasive with a Mohs hardness greater than 6.0 and a velocity of 100-150 m/sec, it has been found that less than 5-10 microns is removed by abrasion and this can be largely replaced by the dopant deposition.

[0046] The impact of the abrasive also acts to roughen and twist the metal surface, thereby embedding and interlocking the dopant into the surface. In order to maximise deposition of the dopant, the Mohs hardness of the abrasive is preferably chosen to be at least 2 levels higher than that of the dopant. This ensures preferential uptake of the dopant and minimal impregnation of the abrasive into the surface. Particularly preferably, the abrasive is at least 3 levels harder than the dopant on the Mohs scale.

[0047] The dopant is found to be chemically bonded to the surface. Given that the reaction happens in ambient atmosphere, it is surprising that there is no evidence of oxide layers between the dopant and the metal. Instead, the dopant is bonded directly to the reactive metal. This ensures excellent adhesion of the dopant to the metal. In addition, the dopant particles are shattered and torn by the impact on the surface and the ongoing abrasive action of the abrasive particle bombardment. For crystalline or semi-crystalline dopant powders, this can produce nano-crystalline dopant particles on the surface, and the resultant high surface energy and reactivity of these sub-micron particles results in materials that bond readily with the metal and which also agglomerate and fuse together on the surface.

[0048] Due to the reactivity induced by the abrasion, high velocities, similar to those found in cold spray, are not required. In addition, the process can occur at ambient temperature and neither the substrate nor the gas stream need be heated as in cold spray. All of the reactions occur at less than 100°C. Although there is no direct heating and it is a room temperature process, the localised heating induced by the kinetic energy of the impact of the particles may be important in localised reactions. For example, during the deposition of polymeric dopants, the localised reactions may give rise to T_G modification of the polymer material.

[0049] Although carried out at low temperatures, the bombardment of the surface does alter the structure of the substrate. Without being bound by theory, aside from the erosion of surface material by the process, microscopic analysis has shown that the abrasive alters the structure of the metal substrate, switching it from coarse grains to fine grains, thereby making it more reactive. The formation of nano-crystallinity also occurs on the substrate side of the interface. Blasting induces a level of Severe Plastic Deformation (SPD) on the substrate and the bombardment thereby increases the dislocation density at the newly exposed surface, which increases the numbers of ultra-fine grains and therefore the overall density of grain boundaries. Grain boundaries provide reaction sites and thus increase the reactivity of a surface. This increase in grain boundary availability increases the reactivity of the metal interface to a depth of 20μm. When combined with the energy transferred from the impacting abrasives and the removal of the passivating oxide layer, this work hardening of the metal could also be expected to enhance the bonding of the dopant to the substrate. In addition, there is no heat affected zone as would be expected from a high energy plasma spray or hot deposition process. This combination of effects gives rise to direct chemical bonding of the dopant to the substrate. In the case of ceramic dopants, this can give rise to a diffusion bonded material. The work hardening also improves the fatigue life of the metal substrate when compared to untreated components.

[0050] The localised reactions also allow for materials to be deposited in an adherent manner which do not normally stick. For example, materials such as PTFE are routinely used as non-stick surfaces as it is notoriously difficult to make PTFE adhere to anything. Despite this, it is possible to deposit an adherent PTFE deposit by mixing PTFE with an angular abrasive and blasting it at a surface. Without being bound by theory, it is possible that the abrasive actually shreds the polymer chain and leaves dangling, unreacted chemical bonds where the chain was cut. Those would provide very reactive sites that could bind to reactive sites on the metal surface and thereby facilitate chemical bonding of the PTFE to the substrate. Because polymeric materials such as PTFE are stable and quite non-reactive, additional energy may be required to induce the reactions that bond the material to the surface. Therefore, when depositing polymeric materials, it may be beneficial to use higher velocity deposition parameters. However, higher velocities require higher gas flows and therefore it is instead preferred to use a larger size abrasive grit to provide additional kinetic energy. If abrasive particles greater than 1500 microns in size are used, then there are insufficient impacts per unit area to bond the polymer to the surface. If small grit particles less than 150 microns in size are used, then the impinging abrasive may lack the kinetic energy to induce reactions with the non-reactive polymer material. When depositing polymeric materials it is therefore preferred to use abrasive particles of 150 to 1500 microns in size, preferably 250 to 1000 microns in size, and most preferably 350 to 750 microns in size as these possess higher kinetic energy and produce enhanced surface abrasion and roughening. However, nowithstanding the above, we have also achieved good deposition of polymer dopants using abrasive particles having an average particle size of the order of 50 microns or smaller, and, separately, using abrasive particles having an average particle size of the order of 13 microns or smaller.

[0051] In addition, when depositing polymeric dopants, the blend of dopant and abrasive should be altered to be rich in abrasive. While standard blasting is carried out with equal mixtures by weight of dopant and abrasive, for polymer dopants it has been found that a ratio of at least 60wt% abrasive and a maximum of 40wt% dopant is preferred. A more preferred ratio comprises at least 70wt% abrasive and no more than 30wt% dopant. In the most preferred ratio, the mixture comprises 80-90wt% abrasive and 10-20wt% dopant. At mixtures above around 90wt% or 95wt% abrasive, there is limited polymer deposition due to excess abrasion, although mixtures having between 90wt% and 95wt% abrasive can advantageously be used to produce (deliberately) a very thin dopant layer.

[0052] Although using a high loading of abrasive in the mixed media and a high average particle size has been beneficial for polymeric dopants, this does not hold true for other dopants. When attempting to deposit ceramics, salts, metals or other materials, it has been found that the particle size of the abrasive is key to producing an optimal coating. While larger abrasive particles give rise to enhanced surface roughness, it has been found that the use of smaller abrasives can give rise to higher surface loadings of dopant. As the loading of the surface is driven by the impaction of the abrasive on the surface, it is preferred to bombard the surface with a large number of smaller particles rather than fewer large particles. This produces more impacts and more surface reactions per unit surface area and thereby facilitates enhanced surface loading of dopant. While deposition of dopant materials can be achieved using abrasives with an average particle size of 500-1000 microns, it has been observed that better results occur with abrasive particles that are less than 500 microns, preferably less than 200 microns, and ideally in the range of 10-150 microns average particle size. In addition, for non-polymeric dopants, the maximum ratio of abrasive to dopant has been found to be 80wt% abrasive to 20wt% dopant, with better loading of the dopant formed when the mixture contains no more than 75wt% abrasive and at least 25wt% dopant. The optimum surface loading of non-polymeric dopants is achieved when the mixture contains no more than 60wt% abrasive and greater than 40wt% dopant. Although a range of abrasive particles have been successfully employed in CoBlast, the average dopant particle is typically in the range of 1-100 microns in size.

[0053] A blend of abrasive sizes may also be used when depositing dopant particles using the CoBlast process. For example, large abrasive particles may be used for surface profile and cleaning effects, simultaneously with small abrasive particles in order to achieve good surface coverage and improved reactivity. For these reasons, and by way of example, we have successfully used a blend of approximately 600 micron and approximately 50 micron alumina abrasive particles when depositing epoxies, zinc phosphate and others as the dopant species.

[0054] In some cases where high surface profile is required it may be most efficient to grit-blast first with large abrasive particles (e.g. having an average particle size of the order of 1500 microns or greater), and then subsequently employ a CoBlast process using small abrasive particles simultaneously with the dopant particles.

[0055] Smaller dopants are more reactive, but larger dopant particles are easier to flow in a powder feeder and are therefore often preferred. In order to commercialise a coating process, the optimal coating may be produced using smaller particles, but the requirement to flow the particles in a smooth and continuous manner from one or more hoppers to the/each delivery nozzle may require the addition of flow agents or the use of larger abrasive or dopant particles. In order to ensure a continuous flow of media from the/each hopper to the/each nozzle it has been found that the mixture of abrasive and dopant should have a Hausner ratio of less than 1.2 (and particularly preferably less than 1.15). For mixtures with a Hausner ratio greater than this value but less than around 1.3-1.5, it is possible to flow the material from a pressure pot as long as the powders are dry, sealed and the total load of powder does not exceed 1.5kg. If the mixture has a Hausner ratio greater than around 1.3-1.5, then it is necessary to physically agitate the mixture using stirring rods, bars, blades or other devices to prevent the powder from compacting and to maintain a constant flow. If the Hausner ratio exceeds around 1.5-1.6, then the maximum load that can be fed from the hopper is 500g in order to ensure that the powder does not compact and block the system. For optimum performance, the hopper should be loaded with no more than 400g of mixed media. In order to ensure a constant supply to the nozzle, it may be beneficial to employ multiple powder feeders each loaded with small quantities of mixed media, preferably less than 500g.

[0056] The Hausner ratio values in the above paragraph are by way of example only, in respect of a specific deposition system we use. For other configurations of the apparatus the Hausner ratio values may differ.

[0057] The deposited CoBlast layer is typically limited to a thin deposit of 2-5 microns, although thicker deposits of up to 10 microns are possible. When attempting to produce thicker deposits, the presence of the abrasive eventually begins to produce excess abrasion and thicker coatings are rapidly removed, meaning that the process is self-limiting with a maximum thickness of 10 microns achievable. In order to deposit thicker coatings, it is beneficial to first deposit a CoBlast layer using a combination of dopant and abrasive. This produces a thin and chemically bonded primer layer onto which additional materials can then be deposited. In a preferred embodiment, the CoBlast process is used to deposit a thin layer of dopant on the surface. The flow of abrasive and dopant is then switched off or redirected and a second bombardment of the surface takes place. This second bombardment can be based on a cold spray process in which additional materials are blasted at the surface with the required critical velocity to adhere the particles to the surface. The benefit of first employing the CoBlast process is that this facilitates the direct chemical bonding of the coating to the metal without an intervening oxide layer and thereby minimises the risk of coating delamination. Alternatively, the second bombardment may be carried out using a mixture of dopant particles and round shot peen particles. The switch from angular abrasive grit to spherical shot peen particles ensures that the secondary process is not dominated by abrasive erosion, and thick coatings can be grown which are anchored to the metal surface by the CoBlast primer layer. This secondary bombardment can be carried out using the same equipment as used in the CoBlast treatment or can comprise a second set of equipment. In a third alternative, the secondary bombardment may involve simply blasting a dopant, without any additional material, at the CoBlast treated surface so as to build up a thicker coating, but without using the high temperatures or high velocity of the cold spray process. This represents a microblast process similar to that described by Ishikawa. The dopant used in any of the secondary bombardment steps may be identical to the dopant used in the CoBlast treatment or it may be different from the CoBlast dopant materials. In each case, the CoBlast layer will act to improve adhesion of the secondary coating by directly bonding the top coat to the metal without any oxide interface. In a preferred method, the top coating is then further processed using thermal, laser, e-beam or some other high energy method in order to cross-link, melt, densify or cure the coating. This also causes the top layer to fuse with the CoBlast primer layer, thereby chemically bonding the top coat directly to the metal substrate.

[0058] Instead of using a bombardment process, the secondary surface treatment may be added using traditional methods such as painting, sputtering, CVD, plasma deposition, ion plating, PVD, ion beam assisted deposition, electron beam PVD, cathodic arc deposition, magnetron sputtering, vacuum evaporation, laser assisted deposition, PECVD, electroplating, spraying, HVOF, powder coating, dip coating, inkjet printing, roller coating, lithography, spin coating or other such technologies. In each case, the initial layer of dopant acts as a primer that allows the top coating to be bound directly to the metal substrate without any intermediate oxide layer. Further curing or heating of the top coat can enhance the bonding to the substrate further.

[0059] There are a wide variety of dopants that can be used in this process. The dopant can comprise materials such as polymers, metals, ceramics (e.g., metal oxides, metal nitrides), and combinations thereof, e.g., blends of two or more thereof.

[0060] Exemplary dopants include modified calcium phosphates, including $Ca_5(PO_4)_3OH$, $CaHPO_4 \cdot 2H_2O$, $CaHPO_4$, $Ca_8H_2(PO_4)_6 \cdot 5H_2O$, α-$Ca_3(PO_4)_2$, β-$Ca_3(PO_4)_2$, tetracalcium phosphate, beta calcium phosphate or any modified calcium phosphate containing carbonate, chloride, fluoride, silicate or aluminate anions, protons, potassium, sodium, magnesium, barium or strontium cations.

[0061] Other dopants include titania (TiO_2), hydroxyapatite, silica, calcium carbonate, biocompatible glass, calcium phosphate glass, carbon, graphite, graphene, chitosan, chitin, barium titanate, zeolites (aluminosilicates), including siliceacous zeolite and zeolites containing at least one component selected from phosphorous, silica, alumina, zirconia.

[0062] In one embodiment, the dopant is a therapeutic agent. The therapeutic agent can be delivered as a particle itself, or immobilized on a carrier material. Exemplary carrier materials include any of the other dopants listed herein (those dopants that are not a therapeutic agent) such as polymers, calcium phosphate, titanium dioxide, silica, biopolymers, biocompatible glasses, zeolite, demineralized bone, de-proteinated bone, allograft bone, and composite combinations thereof.

[0063] Exemplary classes of therapeutic agents include anti-cancer drugs, anti-inflammatory drugs, immunosuppressants, an antibiotic, heparin, a functional protein, a regulatory protein, structural proteins, oligo-peptides, antigenic peptides, nucleic acids, immunogens, and combinations thereof.

[0064] In one embodiment, the therapeutic agent is chosen from antithrombotics, anticoagulants, antiplatelet agents, thrombolytics, antiproliferatives, antiinflammatories, antimitotic, antimicrobial, agents that inhibit restenosis, smooth muscle cell inhibitors, antibiotics, fibrinolytic, immunosuppressive, and anti-antigenic agents.

[0065] Exemplary anticancer drugs include acivicin, aclarubicin, acodazole, acronycine, adozelesin, alanosine, aldesleukin, allopurinol sodium, altretamine, aminoglutethimide, amonafide, ampligen, amsacrine, androgens, anguidine, aphidicolin glycinate, asaley, asparaginase, 5-azacitidine, azathioprine, Bacillus calmette-guerin (BCG), Baker's Antifol (soluble), beta-2'-deoxythioguanosine, bisantrene HCl, bleomycin sulfate, busulfan, buthionine sulfoximine, BWA 773U82, BW 502U83.HCl, BW 7U85 mesylate, ceracemide, carbetimer, carboplatin, carmustine, chlorambucil, chloroquinoxaline-sulfonamide, chlorozotocin, chromomycin A3, cisplatin, cladribine, corticosteroids, Corynebacterium parvum, CPT-11, crisnatol, cyclocytidine, cyclophosphamide, cytarabine, cytembena, dabis maleate, dacarbazine, dactinomycin, daunorubicin HCl, deazauridine, dexrazoxane, dianhydrogalactitol, diaziquone, dibromodulcitol, didemnin B, diethyldithiocarbamate, diglycoaldehyde, dihydro-5-azacytidine, doxorubicin, echinomycin, edatrexate, edelfosine, eflornithine, Elliott's solution, elsamitrucin, epirubicin, esorubicin, estramustine phosphate, estrogens, etanidazole, ethiofos, etoposide, fadrazole, fazarabine, fenretinide, filgrastim, finasteride, flavone acetic acid, floxuridine, fludarabine phosphate, 5-fluorouracil, Fluosol.RTM., flutamide, gallium nitrate, gemcitabine, goserelin acetate, hepsulfam, hexamethylene bisacetamide, homoharringtonine, hydrazine sulfate, 4-hydroxyandrostenedione, hydrozyurea, idarubicin HCl, ifosfamide, interferon alfa, interferon beta, interferon gamma, interleukin-1 alpha and beta, interleukin-3, interleukin-4, interleukin-6, 4-ipomeanol, iproplatin, isotretinoin, leucovorin calcium, leuprolide acetate, levamisole, liposomal daunorubicin, liposome encapsulated doxorubicin, lomustine, lonidamine, maytansine, mechlorethamine hydrochloride, melphalan, menogaril, merbarone, 6-mercaptopurine, mesna, methanol extraction residue of Bacillus calmette-guerin, methotrexate, N-methylformamide, mifepristone, mitoguazone, mitomycin-C, mitotane, mitoxantrone hydrochloride, monocyte/macrophage colony-stimulating factor, nabilone, nafoxidine, neocarzinostatin, octreotide acetate, ormaplatin, oxaliplatin, paclitaxel, pala, pentostatin, piperazinedione, pipobroman, pirarubicin, piritrexim, piroxantrone hydrochloride, PIXY-321, plicamycin, porfimer sodium, prednimustine, procarbazine, progestins, pyrazofurin, razoxane, sargramostim, semustine, spirogermanium, spiromustine, streptonigrin, streptozocin, sulofenur, suramin sodium, tamoxifen, taxotere, tegafur, teniposide, terephthalamidine, teroxirone, thioguanine, thiotepa, thymidine injection, tiazofurin, topotecan, toremifene, tretinoin, trifluoperazine hydrochloride, trifluridine, trimetrexate, tumor necrosis factor, uracil mustard, vinblastine sulfate, vincristine sulfate, vindesine, vinorelbine, vinzolidine, Yoshi 864, zorubicin, and mixtures thereof.

[0066] Exemplary therapeutic agents include immunogens such as a viral antigen, a bacterial antigen, a fungal antigen, a parasitic antigen, tumor antigens, a peptide fragment of a tumor antigen, meta static specific antigens, a passive or active vaccine, a synthetic vaccine or a subunit vaccine. The dopant may be a protein such as an enzyme, antigen, growth factor, hormone, cytokine or cell surface protein.

[0067] The dopant may be a pharmaceutical compound such as an anti-neoplastic agent, an anti-bacterial agent, an anti-parasitic agent, an anti-fungal agent, an analgesic agent, an anti-inflammatory agent, a chemotherapeutic agent, an antibiotic or combinations thereof.

[0068] The dopant could also be growth factors, hormones, immunogens, proteins or pharmaceutical compounds that are part of a drug delivery system such as those immobilized on zeolite or polymeric matrices, biocompatible glass or natural porous apitic templates such as coralline HA, demineralised bone, deproteinated bone, allograft bone, collagen or chitin.

[0069] In one embodiment, the dopant is an anti-inflammatory drug selected from non-steroidal anti-inflammatory drugs, COX-2 inhibitors, glucocorticoids, and mixtures thereof. Exemplary non-steroidal anti-inflammatory drugs include aspirin, diclofenac, indomethacin, sulindac, ketoprofen, flurbiprofen, ibuprofen, naproxen, piroxicam, tenoxicam, tolmetin, ketorolac, oxaprosin, mefenamic acid, fenoprofen, nambumetone, acetaminophen, and mixtures thereof. Exemplary COX-2 inhibitors include nimesulide, NS-398, flosulid, L-745337, celecoxib, rofecoxib, SC-57666, DuP-697, parecoxib sodium, JTE-522, valdecoxib, SC-58125, etoricoxib, RS-57067, L-748780, L-761066, APHS, etodolac, meloxicam, S-2474, and mixtures thereof. Exemplary glucocorticoids include hydrocortisone, cortisone, prednisone, prednisolone, methylprednisolone, meprednisone, triamcinolone, paramethasone, fluprednisolone, betamethasone, dexamethasone, fludrocortisone, desoxycorticosterone, and mixtures thereof.

[0070] Other exemplary therapeutic agents include cell cycle inhibitors in general, apoptosis-inducing agents, antiproliferative/antimitotic agents including natural products such as vinca alkaloids (e.g., vinblastine, vincristine, and vinorelbine), paclitaxel, colchicine, epidipodophyllotoxins (e.g., etoposide, teniposide), enzymes (e.g., L-asparaginase, which systemically metabolizes L-asparagine and deprives cells that do not have the capacity to synthesize their own asparagine); antiplatelet agents such as G(GP) IIb/IIIa inhibitors, GP-IIa inhibitors and vitronectin receptor antagonists; antiproliferative/antimitotic alkylating agents such as nitrogen mustards (mechlorethamine, cyclophosphamide and analogs, melphalan, chlorambucil), ethylenimines and methylmelamines (hexamethylmelamine and thiotepa), alkyl sulfonates-busulfan, nitrosoureas (carmustine (BCNU) and analogs, streptozocin), triazenes--dacarbazine (DTIC); antiproliferative/antimitotic antimetabolites such as folic acid analogs (methotrexate), pyrimidine analogs (fluorouracil, floxuridine, and cytarabine), purine analogs and related inhibitors (mercaptopurine, thioguanine, pentostatin and 2-chlorodeoxyadenosine (cladribine)); platinum coordination complexes (cisplatin, carboplatin), procarbazine, hydroxyurea, mitotane, aminoglutethimide; hormones (e.g., estrogen); anticoagulants (heparin, synthetic heparin salts and other inhibitors of thrombin); fibrinolytic agents (such as tissue plasminogen activator, streptokinase and urokinase), aspirin, dipyridamole, ticlopidine, clopidogrel, abciximab; antimigratory; antisecretory (breveldin); anti-inflammatory: such as adrenocortical steroids (cortisol, cortisone, fluorocortisone, prednisone, prednisolone, 6α-methylprednisolone, triamcinolone, betamethasone, and dexamethasone), non-steroidal agents (salicylic acid derivatives e.g., aspirin; para-aminophenol derivatives e.g., acetominophen; indole and indene acetic acids (indomethacin, sulindac, and etodalac), heteroaryl acetic acids (tolmetin, diclofenac, and ketorolac), arylpropionic acids (ibuprofen and derivatives), anthranilic acids (mefenamic acid, and meclofenamic acid), enolic acids (piroxicam, tenoxicam, phenylbutazone, and oxyphenthatrazone), nabumetone, gold compounds (auranofin, aurothioglucose, gold sodium thiomalate); immunosuppressives: (cyclosporine, tacrolimus (FK-506), sirolimus (rapamycin), azathioprine, mycophenolate mofetil); antigenic agents: vascular endothelial growth factor (VEGF), fibroblast growth factor (FGF); angiotensin receptor blockers; nitric oxide donors; anti-sense oligionucleotides and combinations thereof; cell cycle inhibitors, mTOR inhibitors, and growth factor receptor signal transduction kinase inhibitors; retinoid; cyclin/CDK inhibitors; HMG co-enzyme reductase inhibitors (statins); and protease inhibitors (matrix protease inhibitors).

[0071] In one embodiment, the dopant is an antibiotic chosen from tobramycin, vancomycin, gentamicin, ampicillin, penicillin, cephalosporin C, cephalexin, cefaclor, cefamandole and ciprofloxacin, dactinomycin, actinomycin D, daunorubicin, doxorubicin, idarubicin, penicillins, cephalosporins, and quinolones, anthracyclines, mitoxantrone, bleomycins, plicamycin (mithramycin), mitomycin, polyketide antibiotics such as tetracycline, and mixtures thereof.

[0072] In one embodiment, the dopant is a protein chosen from albumin, casein, gelatin, lysosime, fibronectin, fibrin, chitosan, polylysine, polyalanine, polycysteine, Bone Morphogenetic Protein (BMP), Epidermal Growth Factor (EGF), Fibroblast Growth Factor (bFGF), Nerve Growth Factor (NGF), Bone Derived Growth Factor (BDGF), Transforming Growth Factor-.beta.1 (TGF-.beta.1), Transforming Growth Factor-.beta. (TGF-.beta.), the tri-peptide arginine-glycine-aspartic acid (RGD), vitamin D3, dexamethasone, and human Growth Hormone (hGH), epidermal growth factors, transforming growth factor α, transforming growth factor β, vaccinia growth factors, fibroblast growth factors, insulin-like growth factors, platelet derived growth factors, cartilage derived growth factors, interlukin-2, nerve cell growth factors, hemopoietic cell growth factors, lymphocyte growth factors, bone morphogenic proteins, osteogenic factors, chondrogenic factors, and mixtures thereof.

[0073] In one embodiment, the dopant is a heparin selected from recombinant heparin, heparin derivatives, and heparin analogues or combinations thereof. In one embodiment, the dopant is an oligo-peptide, such as a bactericidal oligo-peptide. In one embodiment, the dopant is an osteoconductive or osteointegrative agent.

[0074] In one embodiment, the dopant is an immunosuppressant, such as cyclosporine, rapamycin and tacrolimus (FK-506), ZoMaxx, everolimus, etoposide, mitoxantrone, azathioprine, basiliximab, daclizumab, leflunomide, lymphocyte immune globulin, methotrexate, muromonab-CD3, mycophenolate, and thalidomide.

[0075] In one embodiment, the carrier material is a polymer such as polyurethanes, polyethylene terephthalate, PLLA-poly-glycolic acid (PGA) copolymer (PLGA), polycaprolactone, poly-(hydroxybutyrate/hydroxyvalerate) copolymer, poly(vinylpyrrolidone), polytetrafluoroethylene, poly(2-hydroxyethylmethacrylate), poly(etherurethane urea), silicones, acrylics, epoxides, polyesters, urethanes, parlenes, polyphosphazene polymers, fluoropolymers, polyamides, polyolefins, and blends and copolymers thereof.

[0076] In one embodiment, the carrier material is a biopolymer selected from polysaccharides, gelatin, collagen, alginate, hyaluronic acid, alginic acid, carrageenan, chondroitin, pectin, chitosan, and derivatives, blends and copolymers thereof.

[0077] In one embodiment, the dopant is a radio opaque material, such as those chosen from alkalis earth metals, transition metals, rare earth metals, and oxides, sulphates, phosphates, polymers and combinations thereof.

[0078] In one embodiment, the dopant is a pigment designed to alter the emission, absorbance or reflectance of a surface. The deposited pigment may comprise part of a thermal control surface.

[0079] In one embodiment, the surface containing the deposited dopant may be electrically conductive. This conductivity may be sufficient to prevent the build-up of electrical static charge on the surface.

[0080] In one embodiment, the dopant is a component present within an adhesive or paint. This component may bind to the adhesive or paint as it cures thereby chemically bonding the top layer to the substrate. Examples of such components include monomers, pre-polymers, pigments, silanes, fillers such as silica or clay . The dopant may be fusion bonded epoxy, including of derivatives of bisphenol A and epichlorohydrin. The dopant may be an epoxy prepolymer or may be derived from bisphenol A, bisphenol F, Novolac, Glycidylamine epoxy resins or aliphatic epoxy resin. The component may be an additive such as accelerators, corrosion inhibitors, adhesion promoters, fire retardants or fungicides. Typical corrosion-inhibiting dopant species that may be used in the present method include but are not limited to a chromate, phosphate, polymer, oxide or a nitride. For example, the dopant may be ceria. In a preferred method, the coating is derived from a phosphate compound. The phosphate may comprise iron phosphate, manganese phosphate, zinc phosphate or combinations thereof. Alternatively, or in addition, a primer-forming dopant species may comprise a silane, siloxane, acrylate, epoxy, hydrogen bonded silicon compound or material which contains one or more vinyl, peroxyester, peroxide, acetate or carboxylate functional group.

[0081] Abrasive species that may be used in the present method (as a second set of particles, delivered substantially simultaneously with the first) include but are not limited to shot or grit made from silica, sand, alumina, zirconia, barium titanate, calcium titanate, sodium titanate, titanium oxide, glass, biocompatible glass, diamond, silicon carbide, boron carbide, dry ice, boron nitride, sintered calcium phosphate, calcium carbonate, metallic powders, carbon fibre composites, polymeric composites, titanium, stainless steel, hardened steel, carbon steel chromium alloys or any combination thereof. The abrasive is chosen to be a different material than the dopant.

[0082] Examples of substrates that may be treated using this technology include metals and intermetallic compounds, such as those metals chosen from pure metals, metal alloys, intermetallics comprising single or multiple phases, intermetallics comprising amorphous phases, intermetallics comprising single crystal phases, and intermetallics comprising polycrystalline phases. Exemplary metals include titanium, titanium alloys (e.g., NiTi or nitinol), ferrous alloys, stainless steel and stainless steel alloys, carbon steel, carbon steel alloys, aluminum, aluminum alloys, nickel, nickel alloys, nickel titanium alloys, tantalum, tantalum alloys, niobium, niobium alloys, chromium, chromium alloys, cobalt, cobalt alloys, magnesium and magnesium alloys, copper and copper alloys, precious metals, and precious metal alloys.

[0083] In one embodiment, the substrate is an implantable medical device. Exemplary medical devices include catheters, guide wires, stents, dental implants, pulse generators, implantable orthopedic, spinal and maxillofacial devices, cochlear implant, needles, mechanical heart valves and baskets used in the removal of pathological calcifications. In the case of biomedical devices it is desirable that the level of impregnation of the abrasive itself in the surface is minimal. The abrasive should further be biocompatible as it is likely that some impregnation will occur.

[0084] In one embodiment, the substrate is a vehicle component, including an automotive chassis, body or panel component, or an aerospace vehicle, satellite, rocket or spacecraft component, or a marine ship or boat component, specifically the outer hull. In one embodiment, the substrate is an engine or an engine component including exhaust outlets.

[0085] The substrate may be an electronic component, including components for use in applications in the Communication Infrastructure, Aerospace and Defence, Automotive, Mobile and Consumer Electronics, and High Speed Digital markets. The electronic components may include circuit boards, cases, housing, switches, terminals, protection devices, transducers, capacitors, resistors, heat exchangers, antennas, human interfaces, dielectrics, thermal control surfaces, power sources or display components.

[0086] In one embodiment, the substrate is a mould such as that used in the manufacture of plastic, silicone, rubber, composite, polymer, clay, glass, metal or ceramic materials. The dopant may be chosen to enhance release of the cast part from the mould and the dopant may comprise a fluoropolymer or silicone material.

[0087] In one embodiment the substrate may be a pipe, tube or storage vessel, specifically one used in the petrochemical, marine, pharmaceutical, chemical, biotech or food and beverage industry. The deposited dopant may be chosen to minimise fouling or build-up of materials on the inside of the container.

[0088] The dopant and abrasive are preferentially mixed together and blasted at a surface. The blasting may be carried out using wheel abrading equipment or fluid based blast equipment. Where fluid blasting is carried out, the fluid may be a gas or a liquid, such as water. Appropriate gases include air, nitrogen, argon, helium, carbon dioxide or mixtures thereof. If using combustible or explosive media, the fluid may comprise water or may be largely composed of an inert gas.

Example 1

[0089] An aluminium sample was electrolytically plated to produce a uniform 12 micron thick metallic Ni layer. This surface was then subjected to a CoBlast surface treatment using alumina as the abrasive and calcium phosphate as the dopant. The powders were pre-mixed and blasted at the surface. As can be seen from the optical micrographs in Figure 4 and the EDX analysis in Figure 5, following the CoBlast treatment the nickel was still evident on the surface of the substrate, indicating that there was less than 12 microns eroded from the substrate surface. In addition, the EDX shows the presence of additional elements attributed to the presence of the calcium phosphate dopant impregnated into the surface. Close examination of the optical micrographs in Figure 4 shows that all of the nickel plating is not removed during the CoBlast treatment. However, it can be seen that there is some level of nickel removal from the surface during CoBlast, based on the cross-sectional analysis. Although the removal rate is not uniform, there is typically 2-10 microns of metal removed. The overall thickness of the substrate does not alter significantly as any metal removal is offset by deposition of the dopant material. It is also clear that the CoBlast treated surface is rougher than the untreated nickel surface.

Example 2

[0090] 150 micron alumina abrasive was mixed with calcium phosphate (Hydroxyapatite or HA, 20-65 micron average particle size) and blasted at a series of grade 2 titanium coupons. The velocity of the bombarding particle was varied from 170-195 m/sec. Samples were then washed and examined using SEM. In each case, the surface was found to be loaded with high levels of calcium and phosphorous, confirming that calcium phosphate had been deposited in each case. Samples were also subjected to XRD analysis. In each case, the analysis detected only peaks associated with titanium and the calcium phosphate deposit. Analysis of the ratio of the intensity of the HA (211) peak to the intensity of the Ti (101) peak showed approximately equivalent signals for all samples.

[0091] The adhesion of the deposited material was measured using a test method based on ASTM F1147. This determined that the adhesion of the deposit was in excess of 58 MPa, which was the failure point of the adhesive.

[0092] This experiment was then repeated, but instead of using angular alumina abrasive, the calcium phosphate was mixed with round shot peening particles made from grade 5 titanium. Initial SEM analysis detected calcium phosphate on the surface, though there appeared to be significantly less material present. This was confirmed by XRD analysis. A comparison of the ratio of the intensity of the HA (211) peak to the intensity of the Ti (101) peak showed significant differences from the result achieved using the alumina abrasive. The Ti peak was significantly more pronounced in the spectra derived from the shot peen samples and was found to be 3-4 times more intense than the HA peak, confirming that significantly less calcium phosphate material was deposited using the spherical shot peen media.

[0093] The maximum adhesion measured for the shot peen samples was also measured and an average value of 25 MPa was recorded. This is significantly below the level measured for the samples deposited using an abrasive, thereby confirming that the samples produced by abrasive blasting had a much stronger adhesive bond to the substrate, as would be expected from a chemically bonded material.

[0094] This data confirms that deposition of a ceramic dopant using abrasive media can be accomplished at lower velocities than are used in cold spray processes and that the shape of the bombarding particle is key. Rough, irregular shaped abrasive particles can assist with the deposition of a dopant in far higher loadings than can be achieved with a spherical shot peen bombardment particle. Furthermore, the abrasive particles enhance the adhesion of the dopant to the substrate.

Example 3

[0095] A series of 1 mm thick Grade 5 titanium samples were subjected to abrasive bombardment using a 50:50 mixture of 100 micron alumina abrasive and hydroxyapatite (25-60 microns particle distribution) and a bombardment height of 41 mm. Particle image velocimetry (PIV) was used to quantify the velocity of the bombarding particles. The samples were subject to bombardment at various particle velocities and the surface of the blasted substrates was then subjected to 5 minutes cleaning in an ultrasonic bath filled with deionised water. The samples were air dried and then analysed using SEM-EDX. Signals arising from lighter element such as carbon and oxygen were not measured and instead the analysis focussed on the heavier elements of Ca, P and Ti.

[0096] At velocities less than 100 m/sec, there was minimal hydroxyapatite detected on the surface of the titanium coupons. At velocities in excess of 100 m/sec, there was significant hydroxyapatite loading of the metal. Samples blasted at a velocity of 115 m/sec had an average loading of calcium + phosphorous of 29%, with the remained of the material comprising titanium. SEM imaging detected significant loading of material on the surface. Increasing the velocity further to 194 m/sec resulted in significantly higher loading of 46% calcium + phosphorous, with the remainder comprising titanium.

Example 4

[0097] Polytetrafluoroethylene (PTFE) was deposited onto a superelastic NiTi wire at ambient temperature using <50 μm and <90 μm alumina with a blend ratio of 50:50 by mass. The CoBlast coated wires were compared to wire treated with PTFE only. The coated samples were examined using a variety of techniques: microscopy, surface roughness, wear testing and flexural tests, for which the results are shown in Figure 6. It can be seen that the CoBlast coated samples (samples (b) and (c) in Figure 6) had an adherent coating with a significant resistance to wear compared to the samples coated with PTFE only (sample (a) in Figure 6). This study indicates that the CoBlast process can successfully be used to deposit thin adherent coatings of PTFE onto the surface of superelastic NiTi.

[0098] Aspects and features of the present disclosure are set out in the following numbered clauses which contain the subject-matter of the claims of the parent European patent application as originally filed:

1. A metal surface treatment method wherein the surface is simultaneously bombarded with a mixture of abrasive particles and dopant particles which are delivered at a velocity in the range of 50-250 m/sec,

and thereby depositing the dopant material on the surface.

2. A method according to clause 1, wherein the particles are delivered at a velocity in the range of 100-200 m/sec.

3. A method according to clause 2, wherein the particles are delivered at a velocity in the range of 120-180 m/sec.

4. A method according to any preceding clause, carried out at ambient temperature.

5. A method according to any preceding clause, wherein the abrasive particles have an irregular or angular morphology.

6. A method according to any preceding clause, where the dopant is directly chemically bonded to the metal surface without any intermediate oxide layer.

7. A method according to any preceding clause, wherein the dopant particles are agglomerated together on the metal surface.

8. A method according to any preceding clause, wherein the abrasive has a hardness greater than 6.0 on the Mohs scale.

9. A method according to clause 8, wherein the abrasive has a hardness of 8.0 or above on the Mohs scale.

10. A method according to any preceding clause, wherein the abrasive has a hardness at least 2 levels higher than that of the dopant on the Mohs scale.

11. A method according to clause 10, wherein the abrasive has a hardness at least 3 levels higher than that of the dopant on the Mohs scale.

12. A method according to any preceding clause, wherein the dopant is a polymer and the abrasive has an average particle size in the range of 5-5000 microns.

13. A method according to clause 12, wherein the abrasive has an average particle size in the range of 5-1500 microns.

14. A method according to clause 13, wherein the abrasive has an average particle size in the range of 10-150 microns.

15. A method according to clause 13, wherein the dopant is a polymer and the abrasive has an average particle size in the range of 150-1500 microns.

16. A method according to clause 15, wherein the abrasive has an average particle size in the range of 250-1000 microns.

17. A method according to clause 16, wherein the abrasive has an average particle size in the range of 350-750 microns.

18. A method according to any of clauses 1 to 11, wherein the dopant is a polymer and the abrasive has an average particle size of greater than 300 microns.

19. A method according to any of clauses 12 to 18, wherein the abrasive constitutes at least 60wt% of the mixture of abrasive and dopant particles.

20. A method according to clause 19, wherein the abrasive constitutes at least 70wt% of the mixture of abrasive and dopant particles.

21. A method according to clause 20, wherein the abrasive constitutes at least 80wt% of the mixture of abrasive and dopant particles.

22. A method according to any of clauses 1 to 11, wherein the dopant is a non-polymeric material and the abrasive has an average particle size of less than 500 microns.

23. A method according to clause 22, wherein the abrasive has an average particle size of less than 200 microns.

24. A method according to clause 23, wherein the abrasive has an average particle size of less than 150 microns.

25. A method according to any of clauses 22 to 24, wherein the dopant constitutes at least 20wt% of the mixture of abrasive and dopant particles.

26. A method according to clause 25, wherein the dopant constitutes at least 25wt% of the mixture of abrasive and dopant particles.

27. A method according to clause 26, wherein the dopant constitutes at least 40wt% of the mixture of abrasive and dopant particles.

28. A method according to any preceding clause, wherein the dopant particles have an average particle size in the range of 1-100 microns.

29. A method according to any preceding clause, wherein less than 10 microns of dopant material are

deposited on the surface.

30. A method according to any preceding clause, wherein at least some of the dopant particles penetrate the metal surface and remain physically impregnated in the metal.

31. A method according to any preceding clause, further comprising applying an additional coating on top of the deposited dopant material.

32. A method according to clause 31, wherein the additional coating is applied through a bombardment technique selected from cold spray, peen plating or m icroblasting.

33. An article having a surface treated by a method according to any preceding clause.

34. A method according to any of clauses 1 to 32, or an article according to clause 33, wherein the surface is at least a part of:

an implantable medical device;
a marine or land-based vehicle;
an aerospace vehicle, satellite, rocket or spacecraft;
an electronic device or component;
a mould; or
a pipe, tube or storage vessel.

35. A method of treating a surface substantially as herein described with reference to and as illustrated in any combination of the accompanying drawings.

36. An article comprising a treated surface substantially as herein described with reference to and as illustrated in any combination of the accompanying drawings.

Claims

1. A metal surface treatment method wherein the surface is simultaneously bombarded with a mixture of abrasive particles and dopant particles which are delivered at a velocity in the range of 50-250 m/sec, thereby depositing the dopant material on the surface;
wherein the dopant is a polymer and the abrasive has an average particle size in the range of 5-5000 microns.

2. A method as claimed in claim 1, wherein the particles are delivered at a velocity in the range of 100-200 m/sec;
for example wherein the particles are delivered at a velocity in the range of 120-180 m/sec.

3. A method as claimed in claim 1 or claim 2, carried out at ambient temperature.

4. A method as claimed in any preceding claim, wherein the abrasive particles have an irregular or angular morphology.

5. A method as claimed in any preceding claim, where the dopant is directly chemically bonded to the metal surface without any intermediate oxide layer.

6. A method as claimed in any preceding claim, wherein the dopant particles are shattered and torn by the impact on the surface and the action of the abrasive particle bombardment.

7. A method as claimed in any preceding claim, wherein the dopant particles are agglomerated together on the metal surface.

8. A method as claimed in any preceding claim, wherein the abrasive has a hardness greater than 6.0 on the Mohs scale;

   optionally wherein the abrasive has a hardness of 8.0 or above on the Mohs scale;
   or wherein the abrasive has a hardness at least 2 levels higher than that of the dopant on the Mohs scale, optionally wherein the abrasive has a hardness at least 3 levels higher than that of the dopant on the Mohs scale.

9. A method as claimed in any preceding claim, wherein the abrasive has an average particle size in the range of 5-1500 microns;

   preferably wherein the abrasive has an average particle size in the range of 150-1500 microns;
   more preferably wherein the abrasive has an average particle size in the range of 250-1000 microns;
   for example wherein the abrasive has an average particle size in the range of 350-750 microns;
   or wherein the abrasive has an average particle size of greater than 300 microns.

10. A method as claimed in any preceding claim, wherein the abrasive constitutes at least 60wt% of the mixture of abrasive and dopant particles;

    optionally wherein the abrasive constitutes at least 70wt% of the mixture of abrasive and dopant particles;
    or wherein the abrasive constitutes at least 80wt% of the mixture of abrasive and dopant particles.

11. A method as claimed in any preceding claim, wherein the dopant particles have an average particle size in the range of 1-100 microns.

12. A method as claimed in any preceding claim, wherein less than 10 microns of dopant material are deposited on the surface.

13. A method as claimed in any preceding claim, wherein the surface is metal, and wherein at least some of the dopant particles penetrate the surface and remain physically impregnated in the metal.

14. A method as claimed in any preceding claim, further comprising applying an additional coating on top of the deposited dopant material;
optionally wherein the additional coating is applied through a bombardment technique selected from cold spray, peen plating or microblasting.

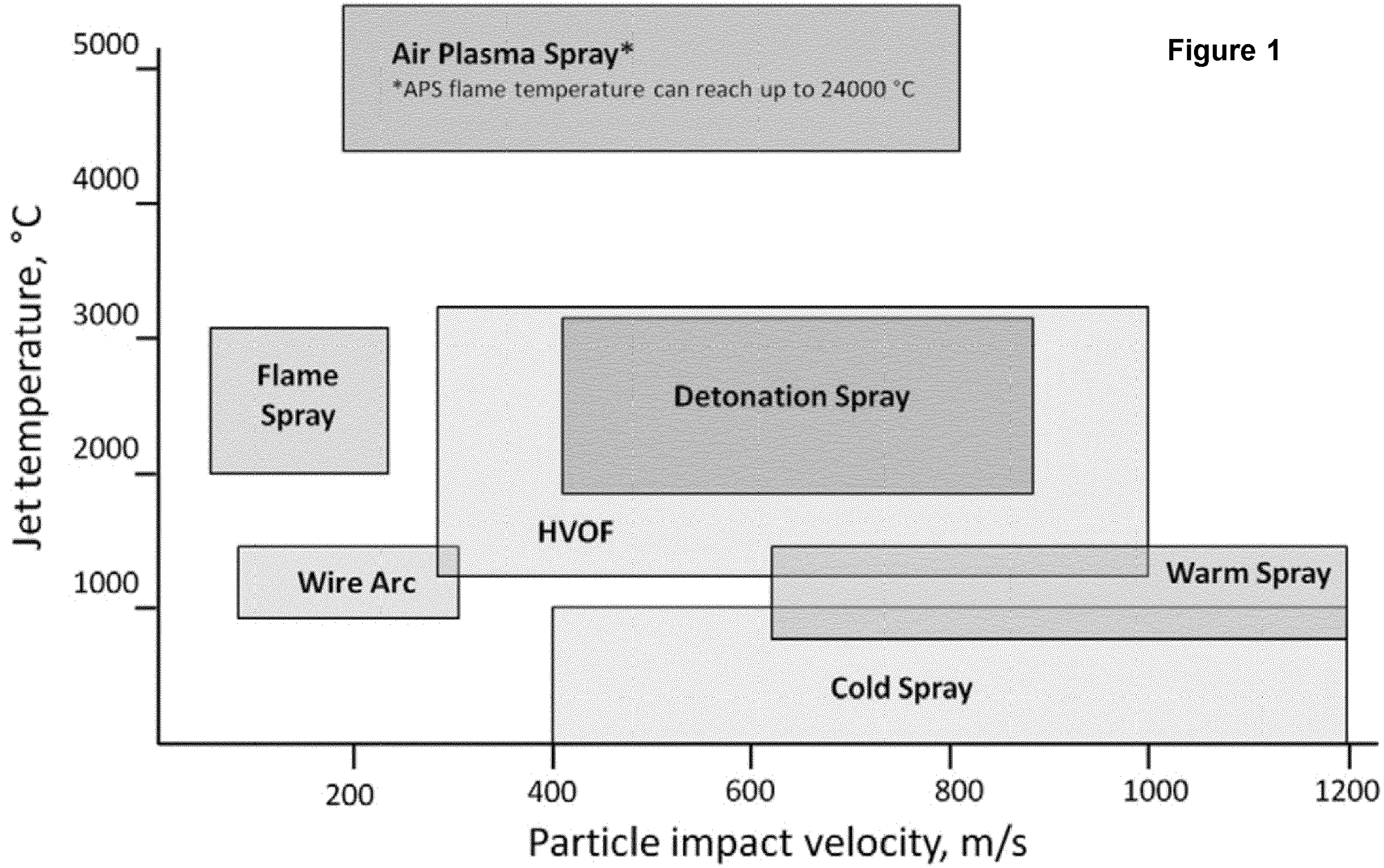
15. A method as claimed in claim 14, further comprising curing or heating the additional coating.

16. An article having a surface treated by a method as claimed in any preceding claim.

17. A method as claimed in any of claims 1 to 15, or an article as claimed in claim 16, wherein the surface is at least a part of:

an implantable medical device;
a marine or land-based vehicle;
an aerospace vehicle, satellite, rocket or spacecraft;
an electronic device or component;
a mould; or
a pipe, tube or storage vessel.

Figure 1


Air Plasma Spray*
*APS flame temperature can reach up to 24000 °C
Flame Spray
Detonation Spray
HVOF
Wire Arc
Warm Spray
Cold Spray
Jet temperature, °C
5000
4000
3000
2000
1000
200
400
600
800
1000
1200
Particle impact velocity, m/s

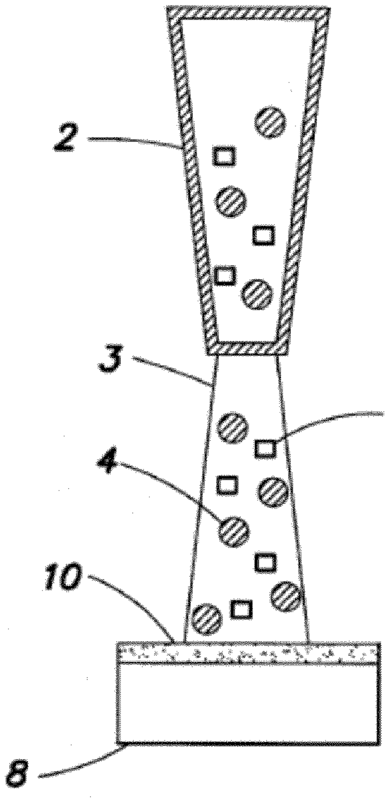


Figure 2a

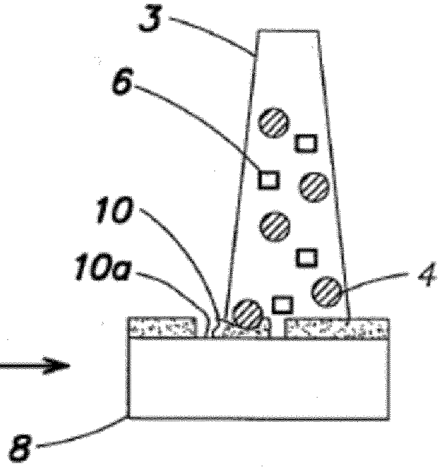


Figure 2b

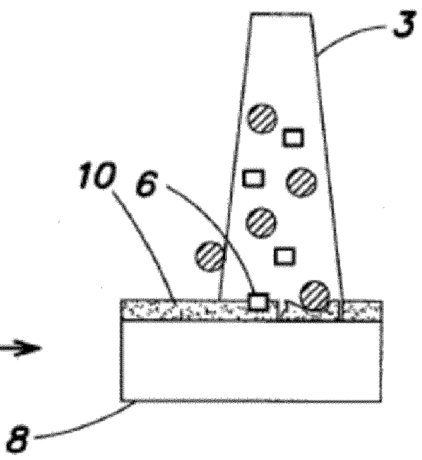


Figure 2c

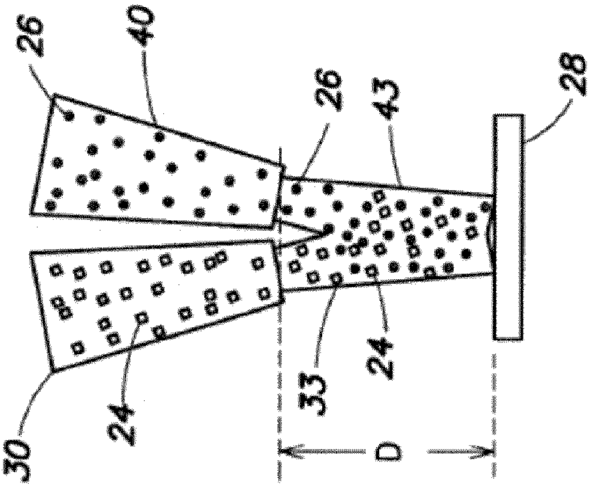


Figure 3c

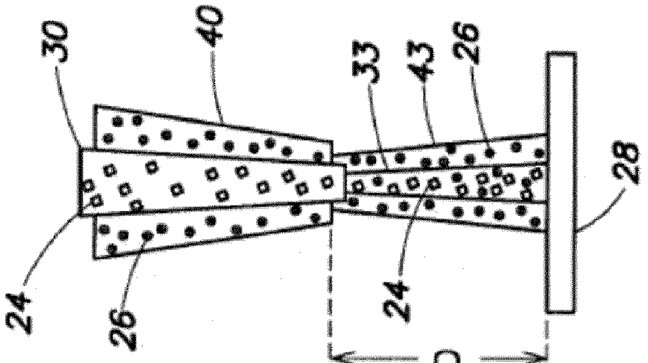


Figure 3b

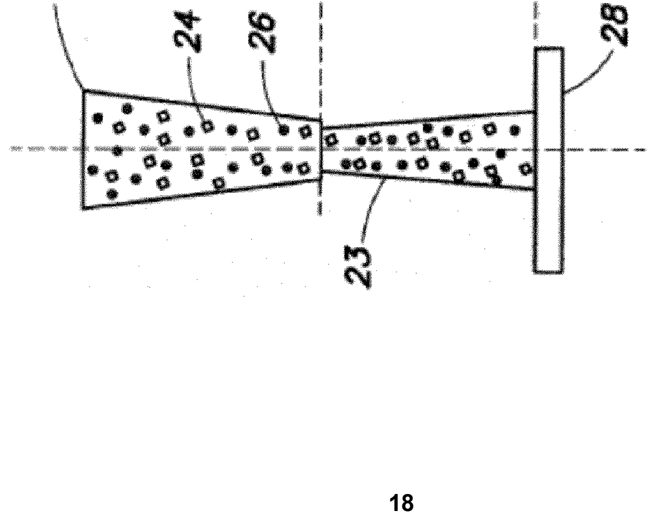


Figure 3a

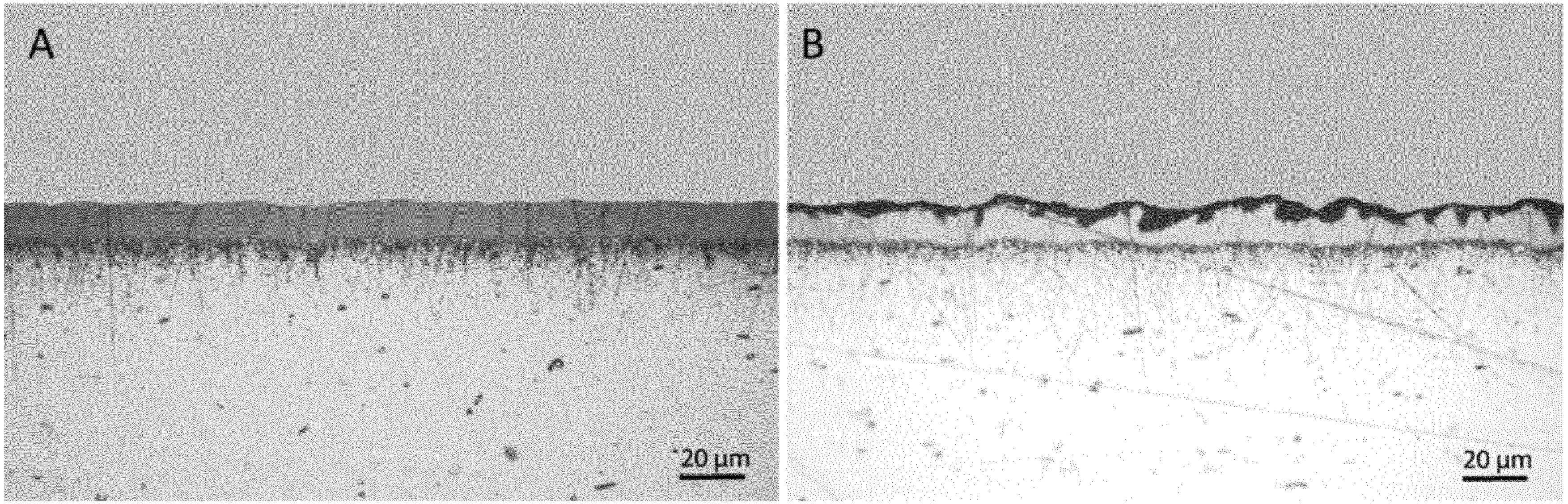


Figure 4

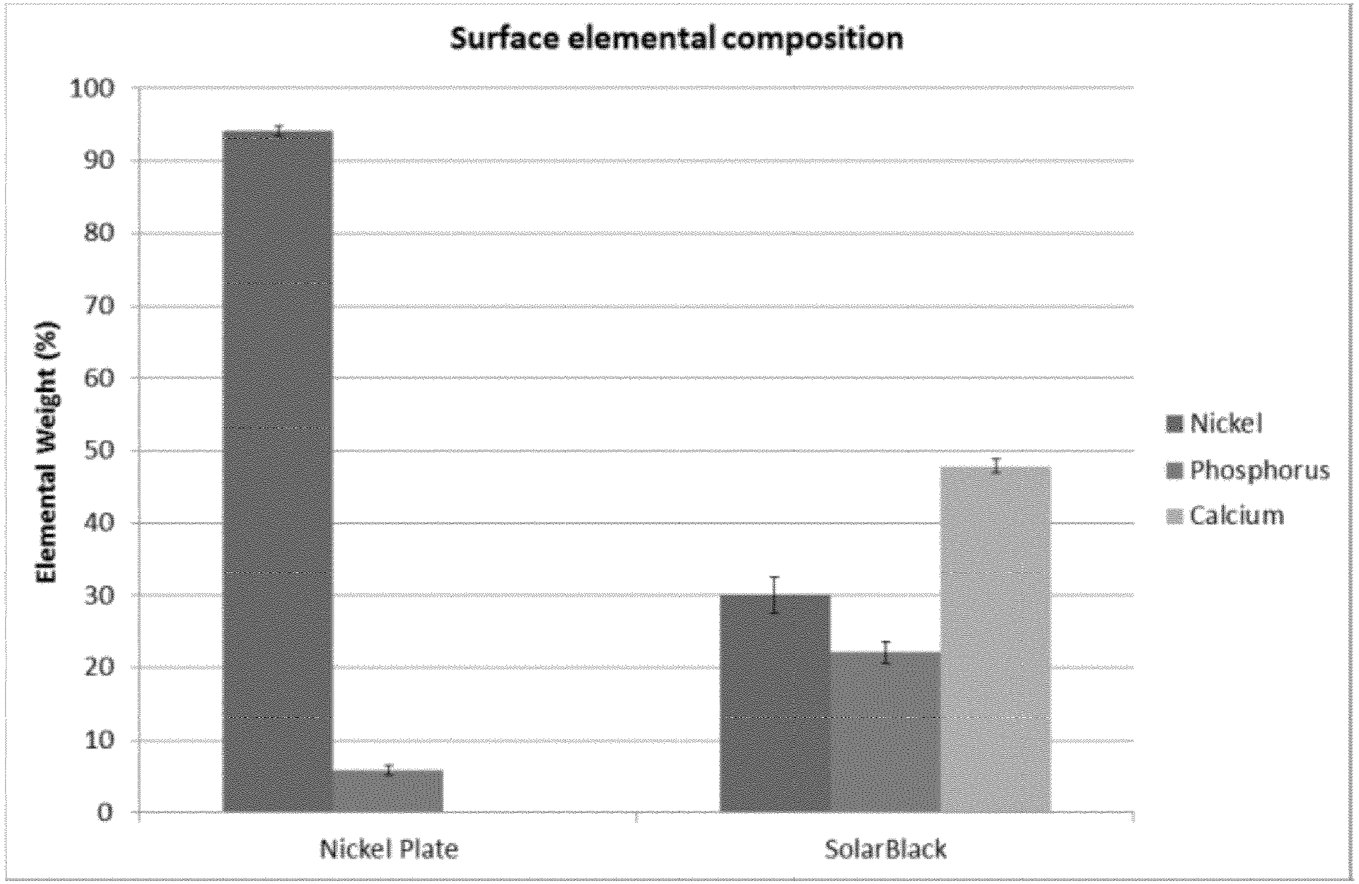

Surface elemental composition
Elemental Weight (%)
100
90
80
70
60
50
40
30
20
10
0
Nickel Plate
SolarBlack
Nickel
Phosphorus
Calcium

Figure 5

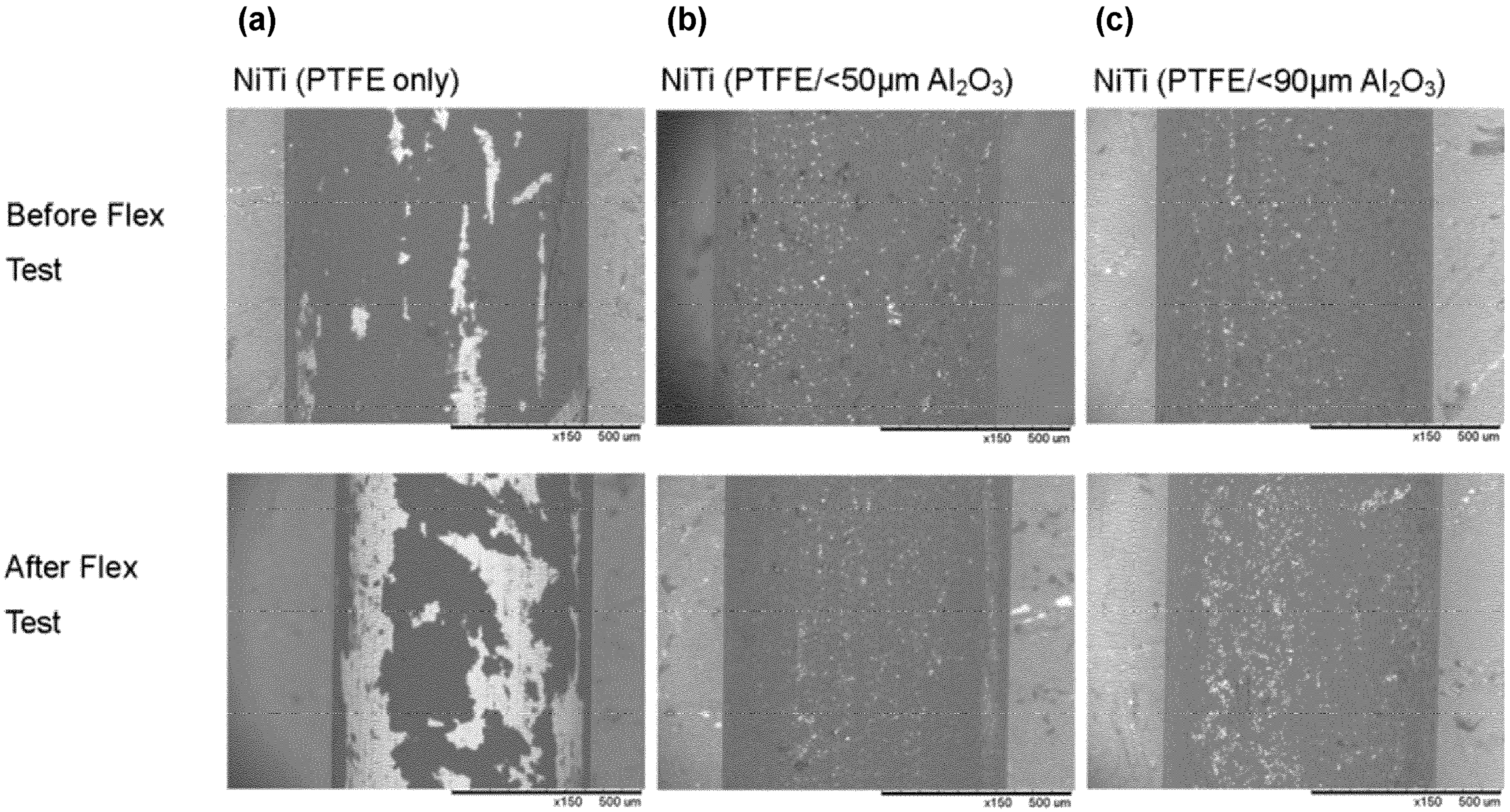

(a)
NiTi (PTFE only)
(b)
NiTi (PTFE/<50µm Al_2O_3)
(c)
NiTi (PTFE/<90µm Al_2O_3)
Before Flex
Test
After Flex
Test
x150 500 um
x150 500 um
x150 500 um
x150 500 um
x150 500 um
x150 500 um

Figure 6

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EUROPEAN SEARCH REPORT

Application Number
EP 21 20 8806

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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1 The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	8 December 2021	Carmichael, Guy

CATEGORY OF CITED DOCUMENTS

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EUROPEAN SEARCH REPORT

Application Number
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Place of search	Date of completion of the search	Examiner
The Hague	8 December 2021	Carmichael, Guy

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Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

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