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(54) Title: AN ARTICLE AND A METHOD OF MAKING AN ARTICLE

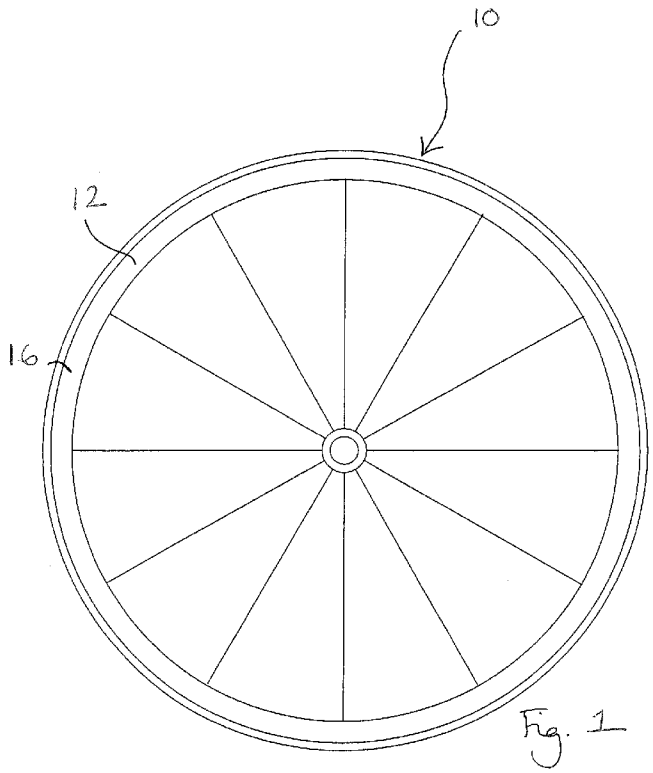

Fig. 1

(57) Abstract: An article, such as a bicycle wheel (10), includes a substrate, at least a surface of the substrate being made of or containing a composite material comprising fibres dispersed in an organic matrix, for example a carbon fibre composite. A thermal sprayed first layer of coating material is provided on the surface, such as the braking area of the rim of the bicycle, the coating material of the first layer wholly comprising inorganic material and including at least one of the group comprising TiO_2, titanate, Al_2O_3 and aluminate.

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An Article and a Method of Making an Article

The invention relates to an article and a method of making an article.

It is known to coat metal parts, for example engine parts, by plasma spraying with a layer of ceramic or metal material. In plasma spraying, the material to be deposited is melted and propelled towards the substrate to be coated. The plasma jet temperature may be of the order of 20,000 K.

According to a first aspect of the present invention there is provided an article, the article including a substrate, at least a surface of the substrate being made of or containing an organic material or a composite material comprising fibres dispersed in an organic matrix, and a thermal sprayed first layer of coating material on the surface, the coating material of the first layer wholly comprising inorganic material and including at least one of the group comprising TiO_2, titanate, Al_2O_3, and aluminate.

It has been found that, surprisingly, TiO_2, titanate, Al_2O_3, and aluminate can be thermally sprayed directly onto an organic or fibre composite material with an organic matrix, without detrimental damage to the material, and that a well adhered coating results.

According to a second aspect of the present invention, there is provided an article, the article including a substrate, at least a surface of the substrate being made of or containing an organic material, a thermal sprayed first layer of coating material on the surface, the coating material of the first layer wholly comprising inorganic material and including at least one of the group comprising TiO_2, titanate, Al_2O_3, and aluminate, the article further comprising a further layer on the first layer.

It has been found that, surprisingly, TiO_2, titanate, Al_2O_3, and aluminate not only can be thermally sprayed directly onto a composite material with an organic matrix, without detrimental damage to the material, but also that the resulting coating forms a very effective bond coat for a further layer.

According to a third aspect of the present invention, there is provided an article, the article including a substrate, at least a surface of the substrate being made of or containing an organic material, and a thermal sprayed first layer of coating material on the surface, and a further layer on the first layer, the coating material of the first layer wholly comprising inorganic material and including at least one of the group comprising TiO_2, titanate, Al_2O_3, and aluminate, the further layer comprising at least 50 wt-% of at least one of zirconia, titania and alumina.

According to a fourth aspect of the present invention, there is provided a bicycle wheel, the bicycle wheel including a rim for a bicycle tyre, the rim including an outer surface wholly or principally of carbon fibre composite material, the wheel including on the outer surface of the rim a thermal sprayed first layer of coating material, the coating material of the first layer wholly comprising inorganic material and including at least one of the group comprising TiO_2, titanate, Al_2O_3, and aluminate.

According to a fifth aspect of the present invention, there is provided a golf club, the head of the golf club being wholly or principally of carbon fibre composite material, at least one of the striking face and the ground engaging face of the golf club including thereon a first layer of coating material, the coating material of the first layer wholly comprising inorganic material and including at least one of the group comprising TiO_2, titanate, Al_2O_3, and aluminate.

According to a sixth aspect of the present invention, there is provided a bone or tooth implant comprising a substrate, the substrate being wholly or principally made of carbon fibre composite material, a surface of the substrate which is arranged to engage bone or tooth when implanted having a thermal sprayed first layer of coating material, the coating material of the first layer wholly comprising inorganic material and including at least one of the group comprising TiO_2, titanate, Al_2O_3, and aluminate.

According to a seventh aspect of the present invention, there is provided a junction box for electromagnetic shielding, the box including a surface wholly or principally of organic or carbon fibre composite material, the box including on the outer surface of the rim a

thermal sprayed first layer of coating material, the coating material of the first layer wholly comprising inorganic material and including at least one of the group comprising TiO_2, titanate, Al_2O_3, and aluminate.

According to an eighth aspect of the present invention, there is provided a carbon fibre composite mould for moulding carbon fibre composite material, the mould comprising an inner surface wholly or principally of carbon fibre composite material, the mould including on its inner surface a thermal sprayed first layer of coating material, the coating material of the first layer wholly comprising inorganic material and including at least one of the group comprising TiO_2, titanate, Al_2O_3, and aluminate.

According to an ninth aspect of the present invention, there is provided a method of coating a substrate surface made of or containing organic material or a composite material comprising fibres dispersed in an organic matrix, the method comprising thermal spraying the surface with a first layer of coating material, the coating material of the first layer wholly comprising inorganic material and including at least one of the group comprising TiO_2, titanate, Al_2O_3, and aluminate.

According to a tenth aspect of the present invention, there is provided a method of coating a substrate surface made of or containing an organic material, the method comprising thermal spraying the surface with a first layer of coating material, the coating material of the first layer wholly comprising inorganic material and including at least one of the group comprising TiO_2, titanate, Al_2O_3, and aluminate, the method further comprising the step of depositing a further layer on the first layer.

According to an eleventh aspect of the present invention, there is provided a method of coating a substrate surface made of or containing an organic material, the method comprising thermal spraying the surface with a first layer of coating material, the coating material of the first layer wholly comprising inorganic material and including at least one of the group comprising TiO_2, titanate, Al_2O_3, and aluminate, and depositing a further layer on the first layer, the further layer comprising at least 50 wt-% of zirconia, titania, and/or alumina.

According to an twelfth aspect of the present invention, there is provided a method of making a bicycle wheel, the bicycle wheel including a rim for a bicycle tyre, the rim including an outer surface wholly or principally of carbon fibre composite material, the method comprising depositing by thermal spraying on the outer surface of the rim a first layer of coating material, the coating material of the first layer wholly comprising inorganic material and including at least one of the group comprising TiO_2, titanate, Al_2O_3, and aluminate.

According to an thirteenth aspect of the present invention, there is provided a method of making a golf club, the head of the golf club being wholly or principally of carbon fibre composite material, the method comprising depositing on at least one of the striking face and the ground engaging face of the golf club a first layer of coating material, the coating material of the first layer wholly comprising inorganic material and including at least one of the group comprising TiO_2, titanate, Al_2O_3, and aluminate.

According to an fourteenth aspect of the present invention, there is provided a method of making a bone or tooth implant comprising a substrate, the substrate being wholly or principally made of carbon fibre composite material, the method comprising thermal spraying a surface of the substrate which is arranged to engage bone or tooth when implanted with a first layer of coating material, the coating material of the first layer wholly comprising inorganic material and including at least one of the group comprising TiO_2, titanate, Al_2O_3, and aluminate, and thermal spraying a top layer of hydroxyapatite.

According to an fifteenth aspect of the present invention, there is provided a method of making a junction box for electromagnetic shielding, the box including a surface wholly or principally of carbon fibre composite material, the method including depositing by thermal spraying a first layer of coating material on the surface, the coating material of the first layer wholly comprising inorganic material and including at least one of the group comprising TiO_2, titanate, Al_2O_3, and aluminate.

According to an sixteenth aspect of the present invention, there is provided a method of making a carbon fibre composite mould for moulding carbon fibre composite

material, the mould comprising an inner surface, the method including depositing by thermal spraying a first layer of coating material on the surface, the coating material of the first layer wholly comprising inorganic material and including at least one of the group comprising TiO_2, titanate, Al_2O_3, and aluminate.

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

Fig. 1 shows a bicycle wheel according to Embodiments 1 and 2 of the present invention;

Fig. 2 is a schematic view in cross section of the rim of Embodiment 1 with a coating layer;

Fig. 3 is a schematic view in cross section of the rim of Embodiment 1 with a coating layer;

Fig. 4 shows a glass fibre epoxy tubes according to Embodiment 3 of the present invention;

Fig. 5 shows a golf club according to Embodiment 4 of the present invention;

Fig. 6 shows the head of the golf club of Fig 5, in fragmentary detail;

Fig. 7 shows a hip prosthesis according to Embodiment 5 of the present invention;

Fig. 8 shows a junction box according to Embodiment 6 or the present invention; and

Fig. 9 shows a mould according to Embodiment 7 of the present invention.

Embodiment 1

A carbon fibre reinforced plastic bicycle wheel 10, as shown in Fig. 1, quickly suffered wear when brakes pads were applied to the rim 12.

A coating layer 14 comprising 100wt-% titania (TiO_2) was plasma sprayed onto the braking area 16, namely the area of the rim to be contacted by a brake block in use. The coating layer was deposited to a thickness of ~50 μm. The plasma spray parameters used were nitrogen 60 slpm, hydrogen 5 slpm, current 400 Amps, carrier

gas 5 slpm, spray distance 100 mm, powder flow 45 g/min, surface speed ~5 ms^{-1} . A schematic view of the rim and coating in cross section is shown in Fig. 2.

The wear resistance of the wheel rim 12 was increased by the coating 14. The adherence of the coating layer 14 to the braking area 14 was better than metal coating layers.

Embodiment 2

A carbon fibre reinforced plastic bicycle wheel 10 was used, the same as that shown in Fig. 1.

A bond coat 18 comprising 100wt-% titania (TiO_2) was plasma sprayed onto the braking area 16. The bond coat 18 was deposited to a thickness of ~50 μm. The plasma spray parameters used were nitrogen 60 slpm, hydrogen 5 slpm, current 400 Amps, carrier gas 5 slpm, spray distance 100 mm, powder flow 45 g/min, surface speed ~5 ms^{-1} .

An Al_2O_3/TiO_2 ceramic layer 20 was then applied on top of the bond coat 18 by plasma spraying. The ceramic layer 20 was applied to a thickness of ~150 μm. The plasma spray parameters used were Nitrogen 60 slpm, hydrogen 5 slpm, current 500 Amps, carrier gas 5 slpm, spray distance 75 mm, powder flow 45 g/min, ceramic powder particle size 50 to 90 micrometres.

A schematic view of the rim and coatings in cross section is shown in Fig. 3.

The wear resistance of the wheel rim 12 was increased by the coatings. The adherence of the bond coat to the braking area 14 was increased compared with metal bond coats.

Embodiment 3

Glass fibre epoxy tubes 22, as shown in Fig. 4, were plasma sprayed on their outer surfaces 24, with a bond coat of Al_2O_3/TiO_2 to a thickness of 50 μm. The plasma spray parameters used were Nitrogen 75 lpm, hydrogen 5 lpm, current 500 Amps, spray distance 75 mm, surface speed ~2 ms^{-1}

An $MgZnO_3$ ceramic layer was then applied on top of the bond coat by plasma spraying, to a thickness of 200 μm. The plasma spray parameters used were Nitrogen 75 lpm, hydrogen 5 lpm, current 500 Amps, spray distance 75 mm, surface speed ~2 ms^{-1}

Embodiment 4

A golf club 30, as shown in Figs. 5 and 6, with a carbon fibre reinforced plastic golf club head 32 was coated with titania ceramic on the striking face 34 of the head 32 and the bottom 36 of the head 32. The spray system was set to work in nitrogen and titania powder feed set to spray at 30 gm/min. Nitrogen flow was preset to 50 litres/min and current to 300 Amps. The robot was programmed to operate a ladder type spray pattern, at a stand off distance of 100 mm from the surface being coated the surface was rotated. In this way, titania bond coat of approximately 25 μm thickness was applied. A second coat was then applied in the same way to provide a layer with a total coating thickness of 50 μm. To avoid impact damage, a 50 μm molybdenum layer was applied to the titania layer, using a Metco™ 9MB plasma spray gun, mounted on a Staubli™ robot, using the following parameters:

Powder feed rate	– 25 g/min
Nitrogen flow	- 80 scfh
Hydrogen flow	- 10 scfh
Current	- 500 A
Spray distance	- 100 mm
Traverse rate	- 150 mm/s

The surface integrity of the ceramic was enhanced by the addition of this thin molybdenum coating, so that if any damage was done to the ceramic, the metal layer would hold it together, preventing spalling.

Embodiment 5

A carbon fibre reinforced plastic hip prosthesis 40, comprising a stem 42 and a ball 44, as shown in Fig. 7, was plasma sprayed with a 150 μm titania layer. A 150 μm hydroxyapatite layer was then plasma sprayed onto the on the surface of the stem 42. The hydroxyapatite coating helped to promote bone ingrowth and enhance the fixation of the implant to the femur.

Embodiment 6

A carbon fibre resin composite junction box 50, as shown in Fig. 8, for electromagnetic shielding in aircraft was coated on its outer surface 52 with a coating layer of Al_2O_3/TiO_2 by plasma spraying. The coating layer 52 provided a tough protective layer for the box without the need for a metal layer.

Embodiment 7

A lightweight mould 60, as shown schematically in Fig. 9, for moulding carbon fibre resin composite structures, for example for large aircraft parts, for example 5m long or more, is made of carbon fibre resin composite. The inner surface 62 of the mould can easily be damaged on removal of the part being moulded.

In this embodiment, the inner surface 62 of the mould 60 was plasma sprayed with a coating layer of Al_2O_3/TiO_2. The ceramic layer provides a tough, wear resistant inner surface for the mould, and prolongs its useful lifespan.

Titania/alumina can be used as a bond coat for an electrically conductive metallic outer layer, the outer layer providing electromagnetic compatibility shielding (EMCS)

with the bond coat providing electrical insulation between the outer layer and the substrate thereby avoiding electrolytic corrosion, spalling and other issues associated with any contact between the metal and substrate.

Titania can be used as a compatible bond coat for the addition of a titania based hard-ceramic outer layer, the latter being used to provide wear resistance. This is applicable to components such as print rollers, in particular lightweight print rollers.

The use of a ceramic (for example, titania/alumina) bond coat, instead of a metal bond, means that coatings can be used on a non-conducting substrate such as carbon composite and plastic in an RF environment.

A bond coat such as a titania/alumina ceramic coating can be used on carbon composite and plastics components where parts are required to be transparent to electromagnetic radiation, eg. mobile communication devices where a hard wearing surface is required on the outside of a structural plastic or composite casing.

Titania and titania/alumina have been proven to be applicable as bond coats on various non-loaded plastics such as PEEK and polyimide.

CLAIMS

1. An article, the article including a substrate, at least a surface of the substrate being made of or containing an organic material or a composite material comprising fibres dispersed in an organic matrix, and a thermal sprayed first layer of coating material on the surface, the coating material of the first layer wholly comprising inorganic material and including at least one of the group comprising TiO_2 , titanate, Al_2O_3 and aluminate.

2. An article according to claim 1, wherein the fibres are one of the group comprising carbon fibres and glass fibres.

3. An article according to claim 1 or claim 2, wherein the organic material or matrix is made of plastics material.

4. An article according to claim 1, 2 or 3 further comprising a further layer on the first layer.

5. An article, the article including a substrate, at least a surface of the substrate being made of or containing an organic material, a thermal sprayed first layer of coating material on the surface, the coating material of the first layer wholly comprising inorganic material and including at least one of the group comprising TiO_2, titanate, Al_2O_3 and aluminate, the article further comprising a further layer on the first layer.

6. An article according to claim 4 or claim 5, wherein the further layer is a thermally sprayed layer.

7. An article according to claim 4, 5 or 6, wherein the further layer is made wholly or principally of ceramic or metal or ceramic and metal.

8. An article according to any of claims 4 to 7, wherein the further layer is wholly or principally made of ceramic material.

9. An article according to any of claims 4 to 8, wherein the further layer is a blend including TiO_2 or titanate and/or Al_2O_3 or aluminate.

10. An article, the article including a substrate, at least a surface of the substrate being made of or containing an organic material, and a thermal sprayed first layer of coating material on the surface, and a further layer on the first layer, the coating material of the first layer including at least one of the group comprising TiO_2, titanate, Al_2O_3 and aluminate, the further layer comprising at least 50 wt-% of zirconia, titania and/or alumina.

11. An article according to any of claims 4 to 10, wherein, the further layer comprises wholly or principally at least one of zirconia, titania, or alumina.

12. An article according to any of claims 4 to 11, wherein the further layer also includes at least one of yttria and magnesia.

13. An article according to any of claims 4 to 12, wherein the level of porosity in the further layer is greater than 5%.

14. An article according to any of claims 4 to 13, wherein the level of porosity in the further layer is at least 15%.

15. An article according to any of claims 4 to 14, wherein the article includes at least one additional layer on the further layer.

16. An article according to claim 15, wherein the or each additional layer is a thermal sprayed layer.

17. An article according to claim 15 or claim 16, wherein the or at least one additional layer is made principally or wholly of ceramic or metal or ceramic and metal.

18. An article as claimed in any of claims 4 to 17, wherein the further layer is at least as thick as the first layer.

19. An article as claimed in any of claims 4 to 18, wherein the further layer is thicker than the first layer.

20. An article as claimed in any of claims 4 to 19, wherein the further layer is at least 100 micrometres thick.

21. An article as claimed in any of claims 4 to 20, wherein the further layer is at least 150 micrometres thick.

22. An article as claimed in any of claims 4 to 21, wherein the further layer is not greater than 300 micrometres thick.

23. An article as claimed in any of claims 4 to 22, wherein the further layer is not greater than 250 micrometres thick.

24. An article according to any preceding claim, wherein the first layer comprises at least 20 wt-% of TiO_2, titanate, Al_2O_3 and/or aluminate.

25. An article according to any preceding claim, wherein the first layer comprises at least 40 wt-% of TiO_2, titanate, Al_2O_3 and/or aluminate.

26. An article according to any preceding claim, wherein the first layer is wholly or principally TiO_2, titanate, Al_2O_3 and/or aluminate.

27. An article according any preceding claim, wherein the coating material of the first layer includes at least one oxide which includes one or more of aluminium, magnesium, calcium, zirconium, and chromium.

28. An article according to any preceding claim, wherein the first layer is up to 300 micrometres in thickness.

29. An article according to any preceding claim, wherein the first layer is up to 250 micrometres in thickness.

30. An article according to any preceding claim, wherein the first layer is greater than 75 micrometres in thickness.

31. An article according to any preceding claim, wherein the first layer is greater than 100 micrometres in thickness.

32. An article according to any preceding claim, wherein the first layer covers the whole of the said surface of the article.

33. An article according to any preceding claim, wherein the article is a bicycle wheel and the first layer is on the braking area of the rim of the wheel.

34. An article as claimed in any of the claims 1 to 32, wherein the article is a golf club and the first layer is on at least one of the striking face and ground engaging face of the golf club.

35. An article according to any of claims 1 to 32, wherein the article is a medical implant.

36. An article according to claim 35, wherein the article is a bone or tooth implant.

37. An article according to claim 35 or claim 36, wherein there is a further layer on the first layer, and the further layer is wholly or principally of titanium.

38. An article according to claim 35, claim 36 or claim 37, wherein there is an additional layer as a top layer which is wholly or principally of hydroxyapatite.

39. A bicycle wheel, the bicycle wheel including a rim for a bicycle tyre, the rim including an outer surface wholly or principally of carbon fibre composite material, the wheel including on the outer surface of the rim a thermal sprayed first layer of coating material, the coating material of the first layer being a blend including at least one of the group comprising TiO_2, titanate, Al_2O_3 and aluminate.

40. A bicycle wheel according to claim 39, further including a further layer, the further layer being wholly or principally of ceramic or metal or ceramic and metal and forming a braking surface to be contacted by a brake block.

41. A bicycle wheel according to claim 40, wherein the further layer is a layer wholly or principally of ceramic.

42. A bicycle wheel according to claim 41, wherein the further layer is at least 50% titanium dioxide.

43. A bicycle wheel according to any of claims 39 to 42, wherein the further layer is a thermal sprayed layer of material with a higher melting point than the melting point of the material of the first layer.

44. A bicycle wheel according to any of claims 39 to 43, wherein the bicycle wheel is wholly or principally of carbon fibre composite material.

45. A golf club, the head of the golf club being wholly or principally of carbon fibre composite material, at least one of the striking face and the ground engaging face of the golf club including thereon a first layer of coating material, the coating material of the first layer including at least one of the group comprising TiO_2, titanate, Al_2O_3 and aluminate.

46. A golf club according to claim 45, further including a further layer, the further layer being wholly or principally molybdenum and/or tungsten.

47. A bone or tooth implant comprising a substrate, the substrate being wholly or principally made of carbon fibre composite material, a surface of the substrate which is arranged to engage bone or tooth when implanted having a thermal sprayed first layer of coating material, the coating material of the first layer including at least one of the group comprising TiO_2, titanate, Al_2O_3 and aluminate.

48. An implant according to claim 47, further including a thermal sprayed top layer of hydroxyapatite.

49. A junction box for electromagnetic shielding, the box including a surface wholly or principally of organic material or a carbon fibre composite material, the box including on the outer surface a thermal sprayed first layer of coating material, the coating material of the first layer including at least one of the group comprising TiO_2, titanate, Al_2O_3 and aluminate.

50. A carbon fibre composite mould for moulding carbon fibre composite material, the mould comprising an inner surface wholly or principally of carbon fibre composite material, the mould including on its inner surface a thermal sprayed first layer of coating material, the coating material of the first layer being a blend including at least one of the group comprising TiO_2, titanate, Al_2O_3 and aluminate.

51. A method of coating a substrate surface made of or containing organic material or a composite material comprising fibres dispersed in an organic matrix, the method comprising thermal spraying the surface with a first layer of coating material, the coating material of the first layer wholly comprising inorganic material and including at least one of the group comprising TiO_2, titanate, Al_2O_3 and aluminate.

52. A method according to claim 51, wherein the fibres are one of glass fibres and carbon fibres.

53. A method according to claim 51 or claim 52, wherein the organic matrix is made of a plastics material.

54. A method according to claim 51or claim 52 further comprising the step of depositing a further layer on the first layer.

55. A method of coating a substrate surface made of or containing an organic material, the method comprising thermal spraying the surface with a first layer of coating material, the coating material of the first layer wholly comprising inorganic material and including at least one of the group comprising TiO_2, titanate, Al_2O_3 and aluminate, the method further comprising the step of depositing a further layer on the first layer.

56. A method according to claim 54 or 55, wherein the further layer is deposited by thermal spraying.

57. A method according to claim 56, wherein the further layer is deposited by plasma spraying.

58. A method according to any of claims 54 to 57, wherein the further layer is wholly or principally made of ceramic or metal or ceramic and metal.

59. A method according to any of claims 54 to 58, wherein the further layer is wholly or principally made of ceramic.

60. A method of coating a substrate surface made of or containing an organic material, the method comprising thermal spraying the surface with a first layer of coating material, the coating material of the first layer including at least one of the group comprising TiO_2, titanate, Al_2O_3 and aluminate, and depositing a further layer on the first layer, the further layer comprising at least 50 wt-% of zirconia, titania, and alumina.

61. A method as claimed in any of claims 54 to 60, wherein the further layer comprises wholly or principally at least one of zirconia, titania, and alumina.

62. A method as claimed in any of claims 54 to 61, wherein the further layer also includes at least one of yttria and magnesia.

63. A method according to any of claims 54 to 62, wherein the method includes depositing at least one additional layer on the further layer.

64. A method according to claim 63, wherein the or each additional layer is deposited by thermal spraying.

65. A method according to claim 64, wherein the or each additional layer is deposited by plasma spraying.

66. A method according to claim 63, claim 64, or claim 65, wherein the or each additional layer is made of ceramic or metal or ceramic and metal.

67. A method according to any of claims 54 to 66, wherein the further layer is deposited to be at least as thick as the first layer.

68. A method according to any of claims 54 to 67, wherein the further layer is deposited to be thicker than the first layer.

69. A method according to any of claims 54 to 68, wherein the further layer is deposited to be at least 100 micrometres thick.

70. A method according to any of claims 54 to 68, wherein the further layer is deposited to be at least 150 micrometres thick.

71. A method according to any of claims 54 to 70, wherein the further layer is deposited to be not greater than 300 micrometres thick.

72. A method according to any of claims 54 to 70, wherein the further layer is deposited to be not greater than 250 micrometres thick.

73. A method according to any of claims 51 to 72, wherein the first layer comprises at least 20 wt-% of TiO_2, titanate, Al_2O_3 and/or aluminate.

74. A method according to claim 73, wherein the first layer comprises at least 40 wt-% of TiO_2, titanate, Al_2O_3 and/or aluminate.

75. A method according to claim 74, wherein the first layer is wholly or principally TiO_2, titanate, Al_2O_3 and/or aluminate.

76. A method according to any of claims 51 to 75, wherein the first layer of coating material is plasma sprayed onto the surface.

77. A method according to claim 76, wherein the first layer of coating material is plasma sprayed in nitrogen.

78. A method according to any of claims 51 to 77, wherein the method includes chemical modification of the surface prior to thermal spraying of the first layer to promote adhesion or reduce substrate outgassing.

79. A method according to any of claims 51 to 78, wherein the method includes temperature treatment of the surface prior to thermal spraying to reduce substrate outgassing.

80. A method according to any of claims 51 to 79, wherein the method includes roughening the substrate surface prior to thermal spraying thereon.

81. A method according to any of claims 5 to 80, wherein the method includes the step of cooling the substrate whilst the first layer is being deposited.

82. A method according to claim 81, wherein the step of cooling the substrate is carried out using an air syphon.

83. A method according to claim 81 or claim 82, wherein the step of cooling the substrate comprises passing an air flow up to $1m^3s^{-1}$ over the substrate.

84. A method according to any of claims 51 to 83, wherein the first layer is sprayed to cover the whole of the said surface of the substrate.

85. A method according to any of claims 51 to 84, wherein the coating material includes at least one oxide which includes one or more of aluminium, magnesium, calcium, zirconium and chromium.

86. A method according to any of claims 51 to 85, wherein the first layer is up to 300 micrometres in thickness.

87. A method according to any of claims 51 to 85, wherein the first layer is up to 250 micrometres in thickness.

88. A method according to any of claims 51 to 87, wherein the first layer is greater than 75 micrometres in thickness.

89. A method according to any of claims 51 to 87, wherein the first layer is greater than 100 micrometres in thickness.

90. A method according to any of claims 51 to 89, wherein the substrate is a bicycle wheel and the first layer is deposited on the area of the rim of the wheel which is frictionally clamped by brake blocks to brake the wheel.

91. A method according to any of claims 51 to 89, wherein the substrate is the head of a golf club and the first layer is deposited on at least one of the striking face and the ground engaging face of the golf club head.

92. A method according to any of claims 51 to 89, wherein the substrate is a medical implant.

93. A method according to claim 92, wherein the substrate is a bone or tooth implant.

94. A method according to claim 92 or claim 93, wherein there is a further layer on the first layer and the further layer is wholly or principally of titanium.

95. A method according to claim 92, claim 93 or claim 94, wherein an additional layer is deposited as a top layer which is wholly or principally of hydroxyapatite.

96. A method according to any of claims 51 to 95, wherein the coating material is sprayed at a rate of 100 g/min or less.

97. A method according to claim 96, wherein the coating material is sprayed at a rate of 70 g/min or less.

98. A method according to claim 97, wherein the coating material is sprayed at a rate of 40 g/min or less.

99. A method according to any of claims 51 to 98, wherein the further layer is sprayed at a rate of 150 g/min or less.

100. A method according to claim 99, wherein the further layer is sprayed at a rate of 100 g/min or less.

101. A method according to claim 100, wherein the further layer is sprayed at a rate of 50 g/min or less.

102. A method of making a bicycle wheel, the bicycle wheel including a rim for a bicycle tyre, the rim including an outer surface wholly or principally of carbon fibre composite material, the method comprising depositing by thermal spraying on the outer

surface of the rim a first layer of coating material, the coating material of the first layer including at least one of the group comprising TiO_2, titanate, Al_2O_3 and aluminate.

103. A method according to claim 102 further including the step of depositing a further layer, the further layer being wholly or principally of ceramic or metal or ceramic and metal and forming a braking surface to be contacted by a brake block.

104. A method according to claim 102, wherein the further layer is a layer wholly or principally of ceramic.

105. A method according to claim 104, wherein the further layer is at least 50% titanium dioxide.

106. A method according to any of claims 102 to 105, wherein the further layer is deposited by thermal spraying.

107. A method according to any of claims 102 to 106, wherein the bicycle wheel is wholly or principally of carbon fibre composite material.

108. A method of making a golf club, the head of the golf club being wholly or principally of carbon fibre composite material, the method comprising depositing on at least one of the striking face and the ground engaging face of the golf club a first layer of coating material, the coating material of the first layer including at least one of the group comprising TiO_2, titanate, Al_2O_3 and aluminate.

109. A method according to claim 108, further comprising the step of depositing a further layer, the further layer being wholly or principally molybdenum and/or tungsten.

110. A method of making a bone or tooth implant comprising a substrate, the substrate being wholly or principally made of carbon fibre composite material, the method comprising thermal spraying a surface of the substrate which is arranged to engage bone or tooth when implanted with a first layer of coating material, the coating material of the first layer including at least one of the group comprising TiO_2, titanate, Al_2O_3 and aluminate, and thermal spraying a top layer of hydroxyapatite.

111. A method of making a junction box for electromagnetic shielding, the box including a surface wholly or principally of carbon fibre composite material, the method including depositing by thermal spraying a first layer of coating material on the surface, the coating material of the first layer including at least one of the group comprising TiO_2, titanate, Al_2O_3 and aluminate.

112. A method of making a carbon fibre composite mould for moulding carbon fibre composite material, the method including depositing by thermal spraying a first layer of coating material on the inner surface of the mould, the coating material of the first layer including at least one of the group comprising TiO_2, titanate, Al_2O_3 and aluminate.

113. A method as claimed in any of claims 51 to 112, wherein the organic material or matrix is a non-loaded plastics material.

114. A method as claimed in claim 113, wherein the organic material or matrix is polyimide and/or PEEK.

115. An article as claimed in any of claims 1 to 38, wherein the organic material or matrix is a non-loaded plastics material.

116. An article as claimed in claim 115, wherein the organic material or matrix is polyimide and/or PEEK.

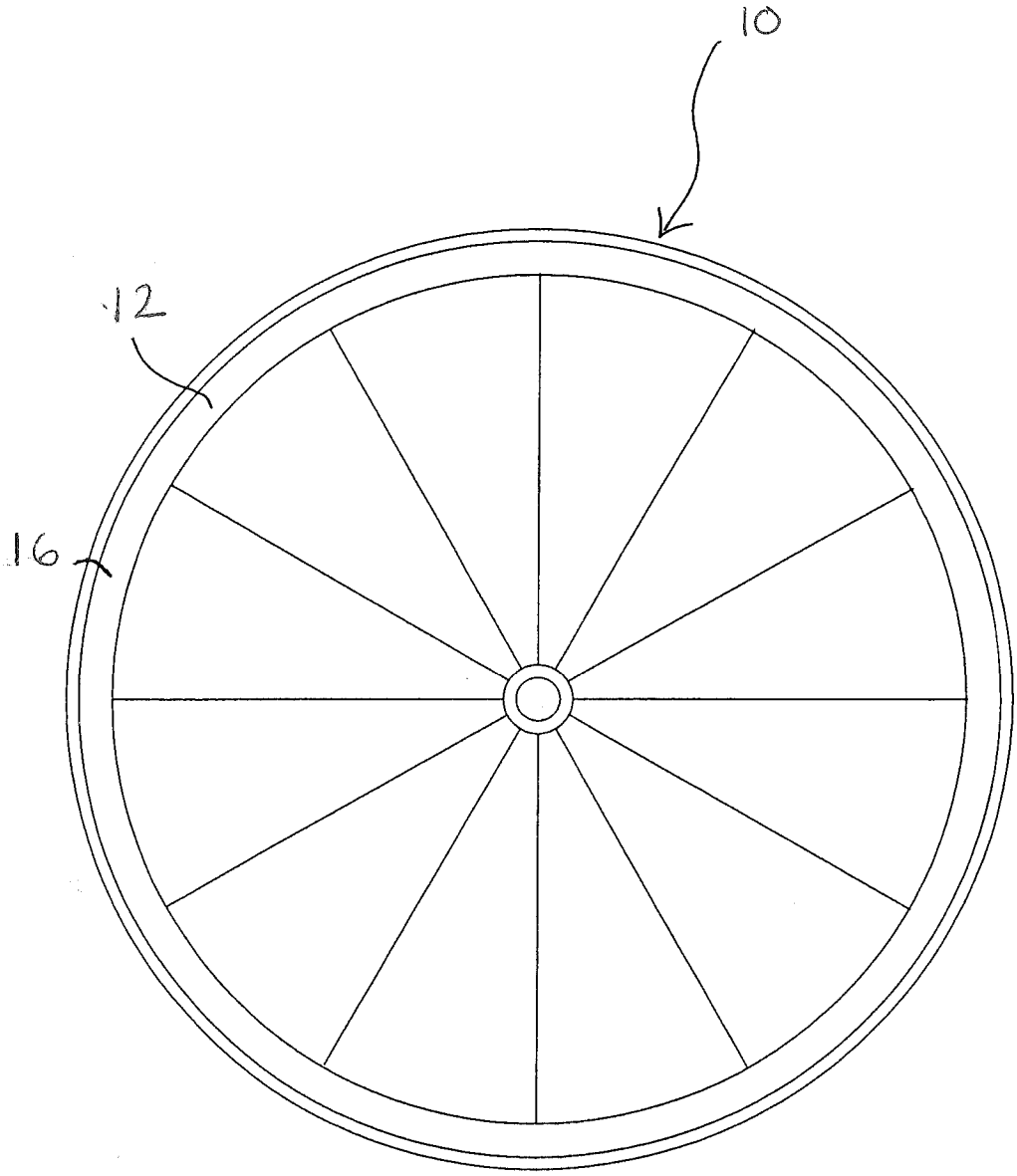


Fig. 1

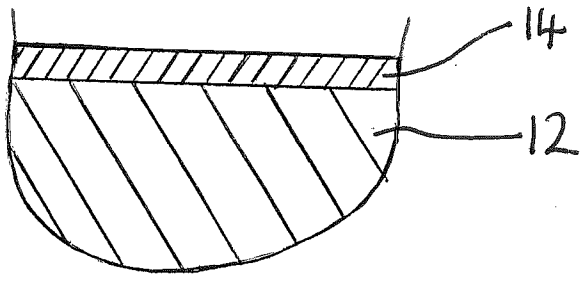


Fig. 2

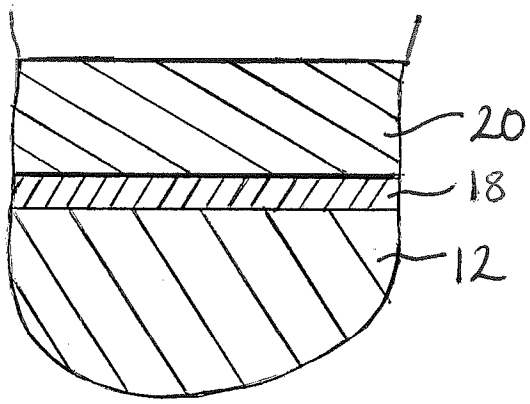


Fig.3

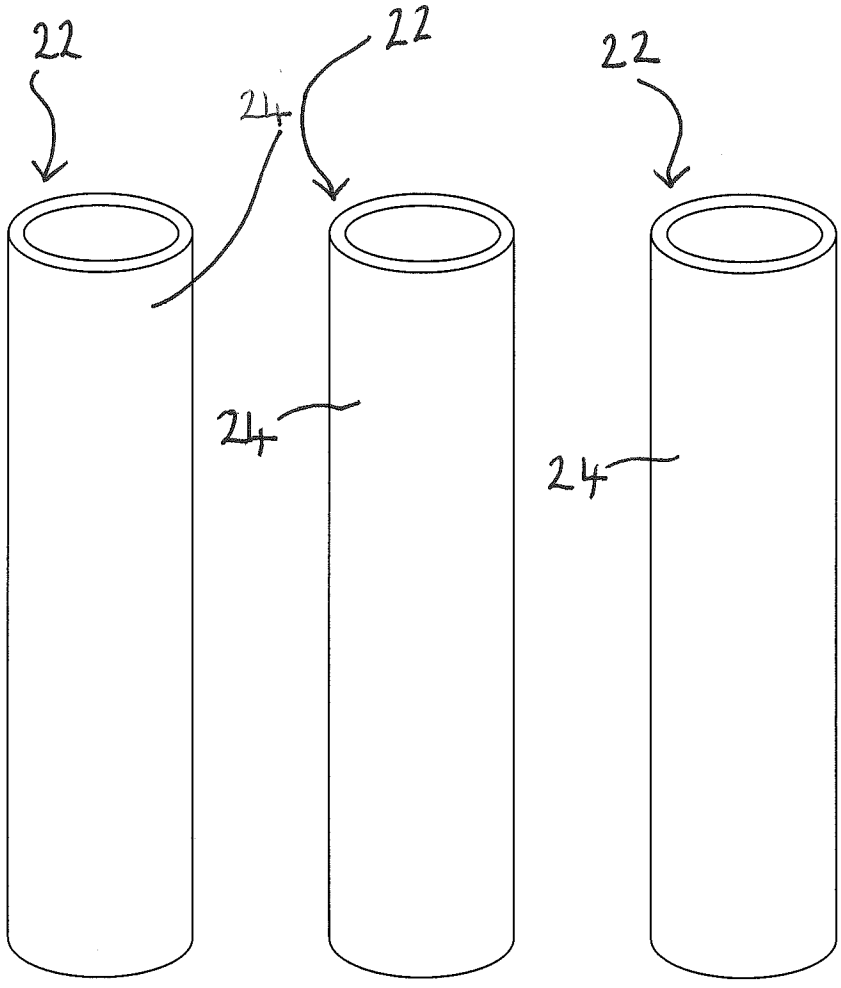


Fig. 4

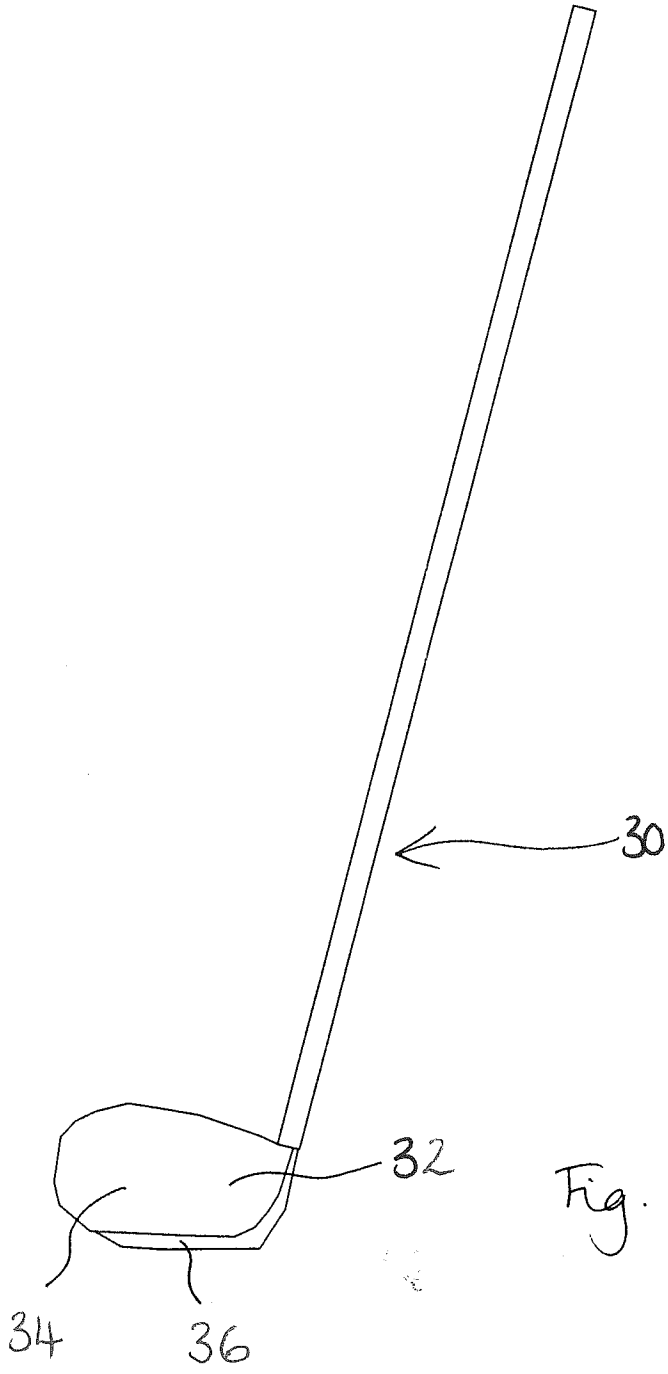
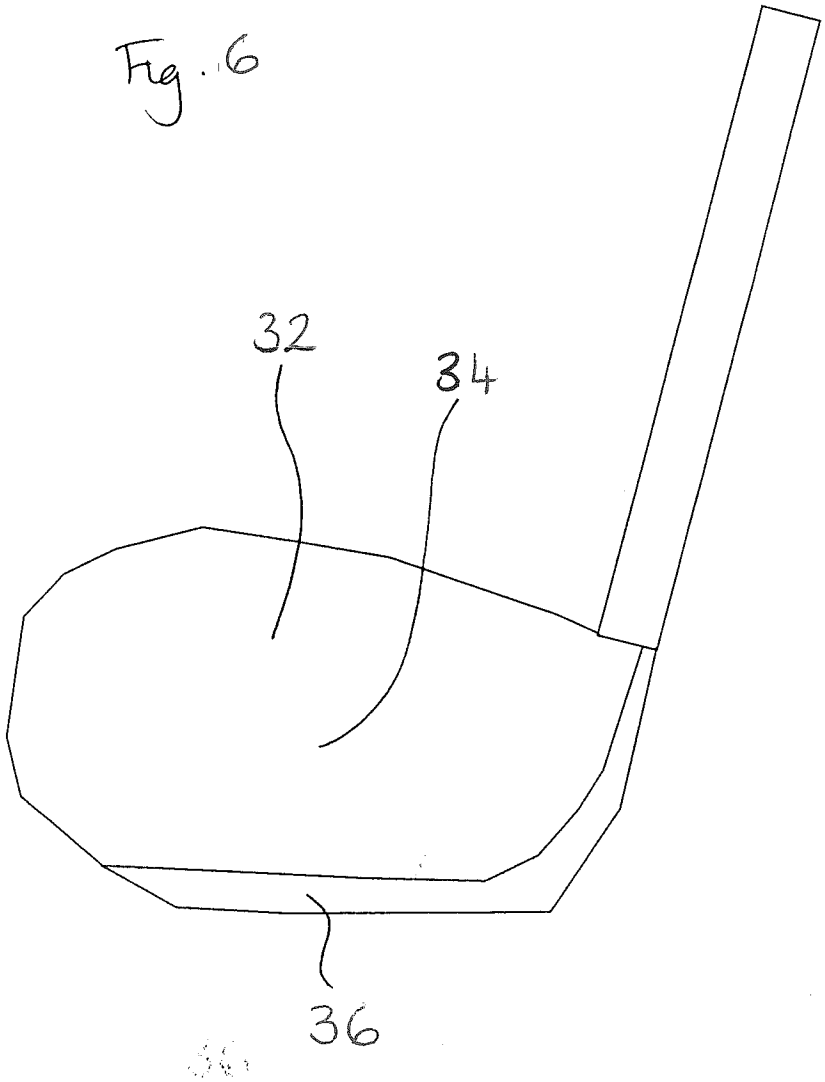


Fig. 5

Fig. 6



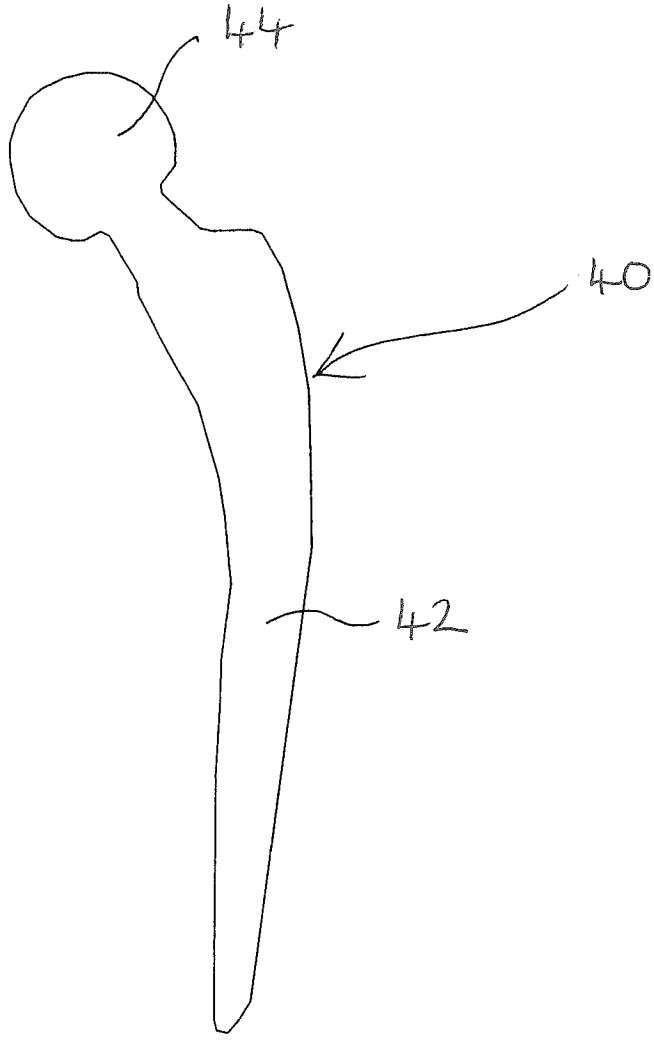


Fig. 7

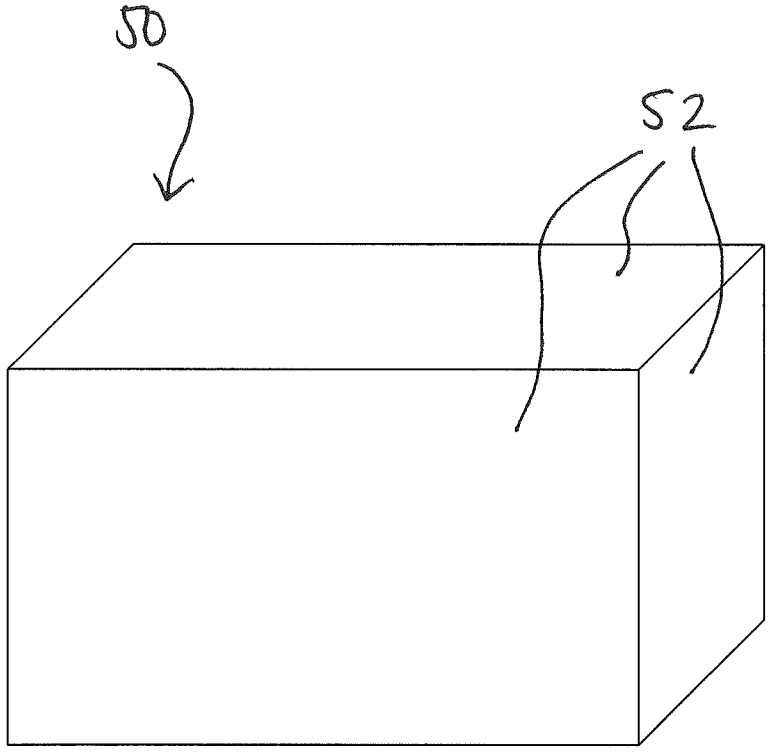


Fig. 8

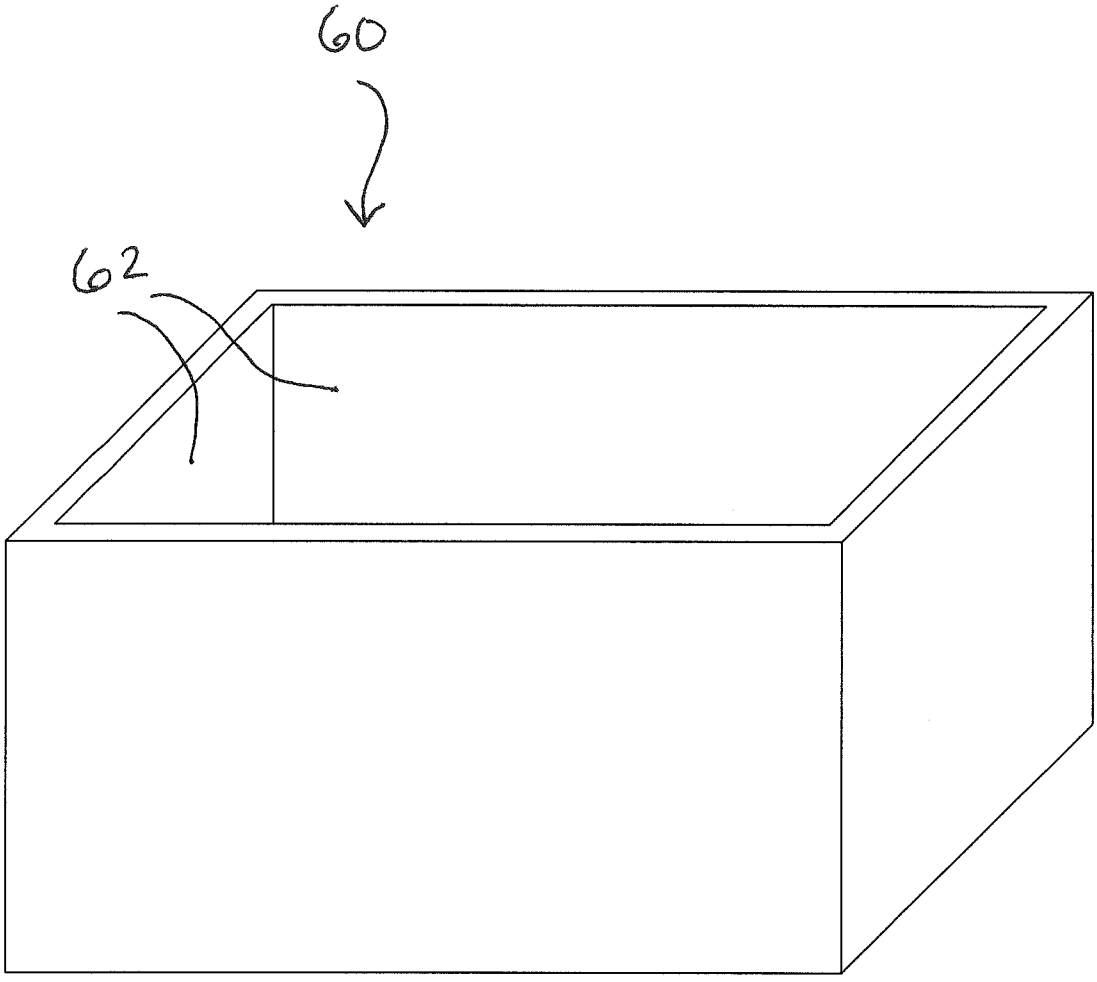


Fig. 9