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## (54) EXPANSIVE COATINGS FOR ANCHORING TO COMPOSITE SUBSTRATES

(57) A method (10) of forming a coated composite article comprises treating a surface of a composite article to form a treated composite article having a plurality of voids in the surface, applying (14) an expansive interface coating to the surface and plurality of voids of the treated composite article to form an intermediate composite article, the expansive interface coating comprising an ex-

pansive alloy, and applying (16) a metallic coating to the intermediate composite article using one of electroless plating, electrolytic plating, and thermal spraying. Each void of at least a subset of the plurality of voids comprises an opening at the surface that is narrower than an inward dimension of the respective void.

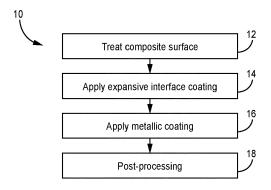


FIG. 1

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#### **BACKGROUND**

**[0001]** The present disclosure relates generally to composite articles and more particularly to application of metallic coatings thereupon.

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**[0002]** Electroplating techniques are not able to produce strongly adherent coatings on composites. Thermal spray processes are generally too hot and can degrade certain types of composite articles. Current pre-plating surface treatment techniques for composite substrates rely on creation of an anchoring mechanism via chemical or mechanical means (e.g., abrasion, grit blasting, chemical etching, etc.) to alter the article surface to provide areas which are more susceptible to intermolecular bonding. Such techniques are considered satisfactory for their intended purpose. However, a need exists for improved techniques resulting in stronger adhesion of plating materials to composite articles.

#### **SUMMARY**

[0003] A method of forming a coated composite article comprises treating a surface of a composite article to form a treated composite article having a plurality of voids in the surface, applying an expansive interface coating to the surface and plurality of voids of the treated composite article to form an intermediate composite article, the expansive interface coating comprising an expansive alloy, and applying a metallic coating to the intermediate composite article using one of electroless plating, electrolytic plating, and thermal spraying. Each void of at least a subset of the plurality of voids comprises an opening at the surface that is narrower than an inward dimension of the respective void.

**[0004]** A treated composite article comprises an outer surface and a plurality of voids formed in the outer surface. Each void of at least a subset of the plurality of voids comprises an opening at the outer surface that is narrower than an inward dimension of the respective void.

#### BRIEF DESCRIPTION OF THE DRAWINGS

## [0005]

FIG. 1 is a flowchart illustrating a method for producing a coated composite article.

FIG. 2 is a simplified cross-sectional view of a composite article after surface treatment.

FIG. 3 is an enlarge cross-sectional view of area A3 of FIG. 2.

FIG. 4 is a simplified cross-sectional view of a composite article after an alternative surface treatment. FIG. 5 is an enlarged cross-sectional view of area A5 of FIG. 4.

FIG. 6 is a simplified cross-sectional view of a coated composite article.

FIG. 7 is a simplified cross-sectional view of an alternative coated composite article.

[0006] While the above-identified figures set forth one or more embodiments of the present disclosure, other embodiments are also contemplated, as noted in the discussion. In all cases, this disclosure presents the invention by way of representation and not limitation. It should be understood that numerous other modifications and embodiments can be devised by those skilled in the art, which fall within the scope of the principles of the invention. The figures may not be drawn to scale, and applications and embodiments of the present invention may include features and components not specifically shown in the drawings.

## **DETAILED DESCRIPTION**

**[0007]** A method of producing a composite article with a metallic coating is disclosed herein. The method includes treating the article's surface to form voids therein, coating the treated surface with an expansive interface coating, and applying a protective and/or decorative metallic coating over the expansive interface coating.

[0008] FIG. 1 is a method flowchart illustrating steps 12-18 of method 10 for producing a coated composite article. FIGS. 2 and 3 are simplified cross-sectional views of a composite article after a surface treatment. FIGS. 4 and 5 are simplified cross-sectional views of the composite article after an alternative surface treatment. FIG. 6 is a simplified cross-sectional view of a coated composite article based on the surface treatment of FIG. 2. FIG. 7 is a simplified cross-sectional view of a coated composite article based on the surface treatment of FIG. 4. FIGS. 2-7 are discussed together with steps 12-18 of method 10.

[0009] The composite article (e.g., composite articles 120, 220 shown and labeled in FIGS. 2 and 4, respectively) can be formed from a polymer-based material (e.g., thermosets, thermoplastics, etc.) in an exemplary embodiment. Other types of composites (e.g., ceramic, glass, etc.) are contemplated herein. At step 12, the composite article can undergo a surface treatment to create surface roughness or voids. Surface treatment can involve the use of a chemical etchant (e.g., acidic or alkali), a mechanical etching process (e.g., routing, milling, grit blasting, laser etching, stamping, etc.), or a combination of the two. Surface treatment can be broadly applied to the article surface, or to targeted regions.

[0010] FIG. 2 is a simplified cross-sectional view of composite article 120 after surface treatment step 12 (i.e., a treated composite article). FIG. 3 is a close-up view of area A3 of FIG. 2. In the state depicted, article 120 includes outer surface 122 and voids 124 formed in surface 122. Voids 124 can be defined by variously disposed straight walls 126 normal to or at an angle relative to surface 122, forming columnar or angled geometries, respectively. An exemplary void 124 includes opening

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128, defined herein as the location at which void 124 meets surface 122. Void 124 can include a first dimension D1, represented by a dashed line and taken at opening 128. Void 124 can further include at least a second dimension D2, also represented by a dashed line and taken inward, based on the orientation of FIGS. 2 and 3, from dimension D1. Dimension D2 can be greater than dimension D1, such that dimension D1 is narrower than at least a section of void 124 inward from opening 128. In the embodiment shown, dimension D2 is the widest dimension of void 124 and dimension D1 is the narrowest. Depending on the cross-sectional shape of void 124 transverse to the view shown in FIGS. 2 and 3, dimensions D1 and D2 can be, for example, a width (i.e., for more quadrilateral shapes), or a diameter (i.e., for circular or elliptical shapes). Voids 124, as shown in FIGS. 2 and 3, can be formed using a mechanical etching process discussed above with respect to step 12. More specifically, voids 124 can be formed via mechanical etching using a tool or laser capable of creating more uniform and repeatable voids 124.

[0011] FIG. 4 is a simplified cross-sectional view of alternative composite article 220 after surface treatment step 12, in particular, employing a chemical etchant. FIG. 5 is a close-up view of area A5 of FIG. 4. Article 220 is substantially similar to article 120, having outer surface 222 and voids 224 formed therein. Article 220 differs in the more irregular shape of voids 224, having walls 226 that can include one or a combination of curved and straight segments. Chemical etching can lead to more irregular voids 224 because etchants tend to follow defects and/or grains within surface 222 of article 220. Voids 224 can further be highly variable with respect to other voids 224 in surface 222. Voids 224 can include opening 228 flush with surface 222. Such voids 224 can accordingly include dimension D3 taken at opening 228, and dimension D4 taken inward of opening 228, based on the orientation of FIGS. 4 and 5. Dimension D4 can be greater than dimension D3, such that dimension D3 is narrower than at least a section of void 224 inward from opening 228. In the embodiment shown, dimension D4 is the widest dimension of void 224 and dimension D3 is the narrowest. Other geometries for voids 124 and/or 224 are contemplated herein.

**[0012]** At step 14, an expansive interface coating can be applied to the treated composite article (e.g., articles 120 and/or 220), forming an intermediate composite article. Suitable coatings can be conductive compounds forming spacious crystal lattices (e.g., with tetrahedral coordination) such that they expand upon cooling to room temperature. Exemplary coating materials can include SAC305 (an alloy of 95.5 % tin, 3% silver, and 0.5% copper), bismuth alloys, and other expansive solder alloys, to name a few non-limiting examples. Expansive interface coating material can be applied to the treated surface by soldering using a wire of the coating material, by pouring a molten material onto the surface, by cold spraying using a powder of the coating material, or by

thermal spraying of a powder of the coating material, to name a few, non-limiting examples. For composites exhibiting thermal risk, such as those formed from certain polymers, molten materials should be below the glass transition temperature  $(T_q)$  of the composite to avoid composite destruction. For composites with higher thermal stability, such as ceramic matrix composites, higher temperature regimes may be reached with the molten materials of the expansive interface coating. The coating material ideally fills voids (i.e., voids 124, 224) in the surface and also coats the surface. Upon cooling, the material expands, exerting a force on the walls of the voids creating an interference fit between the expansive interface coating and the composite article. Because the voids tend to be narrower at the opening than elsewhere within the void, the expansive interface coating essentially becomes anchored to the composite article by its voids. It should be understood that the expansive interface coating need not occupy each void in the surface, nor does it need to fully occupy individual voids to have the intended anchoring effect.

[0013] At step 16, the intermediate composite article can be coated with a protective and/or decorative metallic coating (i.e., plating). Such coating can be applied using an electroless or electrolytic plating technique, thermal spray (e.g., high velocity oxygen fuel or high velocity air fuel), etc. Exemplary coatings can include one or a combination of chromium, cobalt, cobalt-phosphorous, copper, nickel, nickel-phosphorous, nickel-tungsten, tungsten carbide-cobalt, tungsten carbide-cobalt chromium, etc., in a single or multi-layer arrangement. The expansive interface coating of the intermediate composite article creates a more attractive (i.e., conductive) surface, relative to the composite material, upon which the metallic coating materials can deposit.

[0014] FIG. 6 is a cross-sectional view of coated composite article 130, derived from composite article 120 of FIGS. 2 and 3. In an exemplary embodiment, composite article 130 can include expansive interface coating 132 occupying voids 124 and formed upon surface 122 of composite article 120. Coated composite article 130 can further include metallic coating 134 applied over expansive interface coating 132. Coatings 132 and 134 can be formed from any of the materials discussed above with respect to steps 14 and 16, respectively. In an alternative embodiment, expansive coating 132 can occupy voids 124, while some or all of surface 122 remains uncoated by expansive coating 132. In such case, an intermediate, or bridging coating (e.g., copper, nickel, nickel-phosphorous, etc.) can be applied over surface 122 and filled voids 124, and metallic coating 134 can then be applied over the bridging coating.

**[0015]** FIG. 7 is a cross-sectional view of coated composite article 230, derived from composite article 220 of FIGS. 3 and 4. Coated composite article 230 can include expansive interface coating 232 occupying voids 224 and formed upon surface 222 of composite article 220. Coated composite article 230 can further include metallic coat-

ing 234 applied over expansive interface coating 232. Coatings 232 and 234 can be formed from any of the materials discussed above with respect to steps 14 and 16, respectively. Similar to coated article 130, expansive coating 232 can mainly occupy voids 224 in an alternative embodiment, and a bridging coating of copper, nickel, nickel-phosphorous, etc. can be applied over surface 222 prior to the application of metallic coating 234.

**[0016]** At step 18, any desired, but optional post-processing operations can be carried out on the coated article (e.g., coated articles 130, 230). Such operations can include grinding, lapping, machining, and polishing of the metallic coating, the application of additional protective coatings, etc. The disclosed method can be used to coat composites for various purposes, including aerospace, industrial, and other transportation applications.

#### Discussion of Possible Embodiments

**[0017]** The following are non-exclusive descriptions of possible embodiments of the present invention.

[0018] A method of forming a coated composite article comprises treating a surface of a composite article to form a treated composite article having a plurality of voids in the surface, applying an expansive interface coating to the surface and plurality of voids of the treated composite article to form an intermediate composite article, the expansive interface coating comprising an expansive alloy, and applying a metallic coating to the intermediate composite article using one of electroless plating, electrolytic plating, and thermal spraying. Each void of at least a subset of the plurality of voids comprises an opening at the surface that is narrower than an inward dimension of the respective void.

**[0019]** The method of the preceding paragraph can optionally include, additionally and/or alternatively, any one or more of the following features, configurations and/or additional components:

**[0020]** In the above method, the step of treating the surface can include at least one of a chemical etching process and a mechanical etching process.

**[0021]** In any of the above methods, the step of applying the expansive interface coating can include one of soldering using a wire of the expansive alloy, pouring the expansive alloy in a molten form, cold spraying the expansive alloy as a powder, and thermal spraying the expansive alloy as a powder.

**[0022]** In any of the above methods, a temperature of the expansive alloy in the molten form can be less than a glass transition temperature of the composite article.

**[0023]** In any of the above methods, the step of applying the expansive interface coating can further include allowing the expansive interface coating to cool such that it expands and exerts a force against walls of each of the plurality of voids.

**[0024]** In any of the above methods, the expansive alloy can include SAC305 or a bismuth alloy.

[0025] In any of the above methods, the metallic coat-

ing can include one or a combination of cobalt, cobaltphosphorous, copper, nickel, nickel-phosphorous, nickel-tungsten, tungsten carbide-cobalt, or tungsten carbide-cobalt chromium.

**[0026]** In any of the above methods, the composite article can be formed from a polymer-based material.

**[0027]** A treated composite article comprises an outer surface and a plurality of voids formed in the outer surface. Each void of at least a subset of the plurality of voids comprises an opening at the outer surface that is narrower than an inward dimension of the respective void.

**[0028]** The treated composite article of the preceding paragraph can optionally include, additionally and/or alternatively, any one or more of the following features, configurations and/or additional components:

**[0029]** In the above treated composite article, each void of at least the subset of the plurality of voids can further include at least one straight wall normal to or at an angle relative to the outer surface.

**[0030]** In any of the above treated composite articles, each void of at least the subset of the plurality of voids can have a columnar geometry.

**[0031]** In any of the above treated composite articles, each void of at least the subset of the plurality of voids can further include at least one curved wall.

**[0032]** In any of the above treated composite articles, each void of at least the subset of the plurality of voids can have a different geometry than a remainder of the plurality of voids.

[0033] In any of the above treated composite articles, the composite can be a polymer-based material.

**[0034]** In any of the above treated composite articles, the composite can be a ceramic or glass material.

**[0035]** An intermediate composite article can include any of the above treated composite articles and an expansive interface coating applied to the outer surface and the plurality of voids. The expansive interface coating can include an expansive alloy.

**[0036]** In the above intermediate composite article, the expansive interface coating can exert force on at least one wall of each of the plurality of voids.

**[0037]** In any of the above intermediate composite articles, the expansive alloy can include SAC305 or a bismuth alloy.

**[0038]** A coated composite article can include any of the above intermediate composite articles and a metallic coating applied to the expansive interface coating.

**[0039]** In the above coated composite article, the metallic coating can include cobalt, cobalt-phosphorous, copper, nickel, nickel-phosphorous, nickel-tungsten, tungsten carbide-cobalt, or tungsten carbide-cobalt chromium.

**[0040]** While the invention has been described with reference to an exemplary embodiment(s), it will be understood by those skilled in the art that various changes may be made and equivalents may be substituted for elements thereof without departing from the scope of the invention. In addition, many modifications may be made

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to adapt a particular situation or material to the teachings of the invention without departing from the essential scope thereof. Therefore, it is intended that the invention not be limited to the particular embodiment(s) disclosed, but that the invention will include all embodiments falling within the scope of the appended claims.

## Claims

**1.** A method (10) of forming a coated composite article (130, 230), the method comprising:

treating (12) a surface (122, 222) of a composite article to form a treated composite article (120, 220) having a plurality of voids (124, 224) in the surface (122, 222);

applying (14) an expansive interface coating (132, 232) to the surface and plurality of voids of the treated composite article to form an intermediate composite article, the expansive interface coating comprising an expansive alloy; and applying (16) a metallic coating (134, 234) to the intermediate composite article using one of electroless plating, electrolytic plating, and thermal spraying;

wherein each void of at least a subset of the plurality of voids comprises an opening at the surface that is narrower than an inward dimension of the respective void.

- The method of claim 1, wherein the step of treating (12) the surface (122, 222) comprises at least one of a chemical etching process and a mechanical etching process.
- 3. The method of claim 1 or 2, wherein the step of applying (14) the expansive interface coating (132, 232) comprises one of:

soldering using a wire of the expansive alloy; pouring the expansive alloy in a molten form; cold spraying the expansive alloy as a powder; and

thermal spraying the expansive alloy as a powder.

- 4. The method of claim 3, wherein a temperature of the expansive alloy in the molten form is less than a glass transition temperature of the composite article, and/or wherein the step of applying the expansive interface coating further comprises: allowing the expansive interface coating to cool such that it expands and exerts a force against walls of each of the plurality of voids (124, 224).
- **5.** The method of any preceding claim, wherein the expansive alloy comprises SAC305 or a bismuth alloy;

and/or

wherein the metallic coating comprises one or a combination of cobalt, cobalt-phosphorous, copper, nickel, nickel-phosphorous, nickel-tungsten, tungsten carbide-cobalt, or tungsten carbide-cobalt chromium.

- **6.** The method of any preceding claim, wherein the composite article is formed from a polymer-based material.
- **7.** A treated composite article (120, 220) comprising:

an outer surface (122, 222); and a plurality of voids (124, 224) formed in the outer surface;

wherein each void of at least a subset of the plurality of voids comprises an opening at the outer surface that is narrower than an inward dimension of the respective void.

8. The treated composite article of claim 7, wherein each void (124) of at least the subset of the plurality of voids further comprises at least one straight wall normal to or at an angle relative to the outer surface, optionally

wherein each void of at least the subset of the plurality of voids has a columnar geometry.

- 9. The treated composite article of claim 7, wherein each void (224) of at least the subset of the plurality of voids further comprises at least one curved wall, optionally
- wherein each void of at least the subset of the plurality of voids has a different geometry than a remainder of the plurality of voids.
  - **10.** The treated composite article of any of claims 7 to 9, wherein the composite is a polymer-based material.
  - **11.** The treated composite article of any of claims 7 to 9, wherein the composite is a ceramic or glass material.
  - **12.** An intermediate composite article comprising:

the treated composite article of any of claims 7 to 11; and

an expansive interface coating (132, 232) applied to the outer surface and the plurality of voids, the expansive interface coating comprising an expansive alloy.

55 13. The intermediate composite article of claim 12, wherein the expansive interface coating exerts force on at least one wall of each of the plurality of voids.

- **14.** The intermediate composite article of claim 12 or 13, wherein the expansive alloy comprises SAC305 or a bismuth alloy.
- **15.** A coated composite article (130, 230) comprising:

the intermediate composite article of any of claims 12 to 14; and a metallic coating (134, 234) applied to the expansive interface coating, optionally wherein the metallic coating comprises: cobalt, cobalt-phosphorous, copper, nickel, nickel-phosphorous, nickel-tungsten, tungsten carbide-cobalt, or tungsten carbide-cobalt chromium.

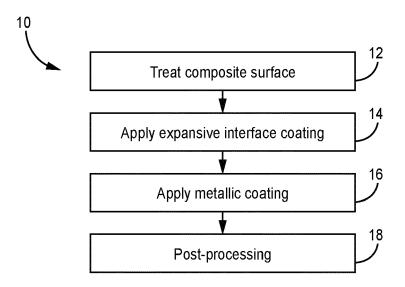


FIG. 1

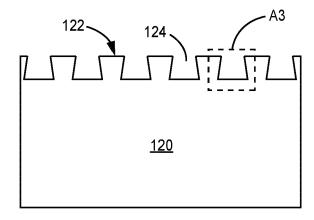


FIG. 2

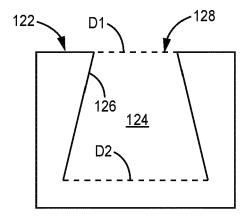


FIG. 3

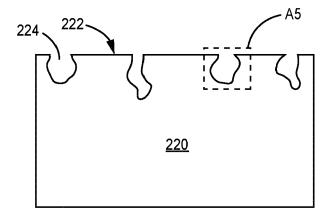


FIG. 4

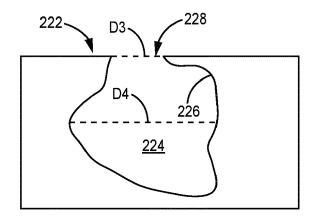


FIG. 5

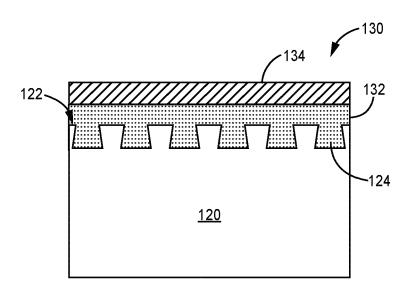
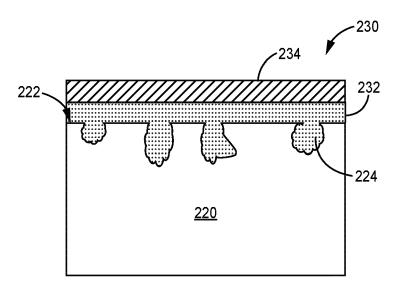


FIG. 6



**FIG. 7** 

**DOCUMENTS CONSIDERED TO BE RELEVANT** 

Citation of document with indication, where appropriate,

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## **EUROPEAN SEARCH REPORT**

**Application Number** 

EP 23 19 5692

CLASSIFICATION OF THE APPLICATION (IPC)

INV.

C23C4/02

C23C4/18 C23C18/16

C23C18/31

TECHNICAL FIELDS SEARCHED (IPC)

C23C в32в C25D C04B

Examiner

Telias, Gabriela

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Relevant

to claim

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CATEGORY OF CITED DOCUMENTS	
X : particularly relevant if taken alone Y : particularly relevant if combined with ano document of the same category A : technological background O : non-written disclosure P : intermediate document	ther

Place of search

Т	: theory o	r 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

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Date of completion of the search

31 January 2024

<sup>&</sup>amp; : member of the same patent family, corresponding document

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# ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

31-01-2024

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