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(54) MANUFACTURING LINE, PROCESS, AND SINTERED ARTICLE

(71) Applicant: CORNING INCORPORATED, CORNING, NY (US)

(72) Inventors: **Michael Edward Badding**, Campbell, NY (US); **William Joseph Bouton**, Big Flats, NY (US); **Jacqueline Leslie Brown**, Lindley, NY (US); **Timothy Joseph Curry**, Orchard Park, NY (US); **Roman E Hurny**, West Seneca, NY (US); **Lanrik Wayne Kester**, Savona, NY (US); **Thomas Dale Ketcham**, Horseheads, NY (US); **John Albert Olenick**, Buffalo, NY (US); **Kathleen Ritter Olenick**, Buffalo, NY (US); **Jeremy Paananen**, Middleport, NY (US); **Thomas Silverblatt**, Amherst, NY (US); **Dell Joseph St Julien**, Watkins Glen, NY (US); **Viswanathan Venkateswaran**, Williamsville, NY (US); **Nathan Michael Zink**, Painted Post, NY (US)

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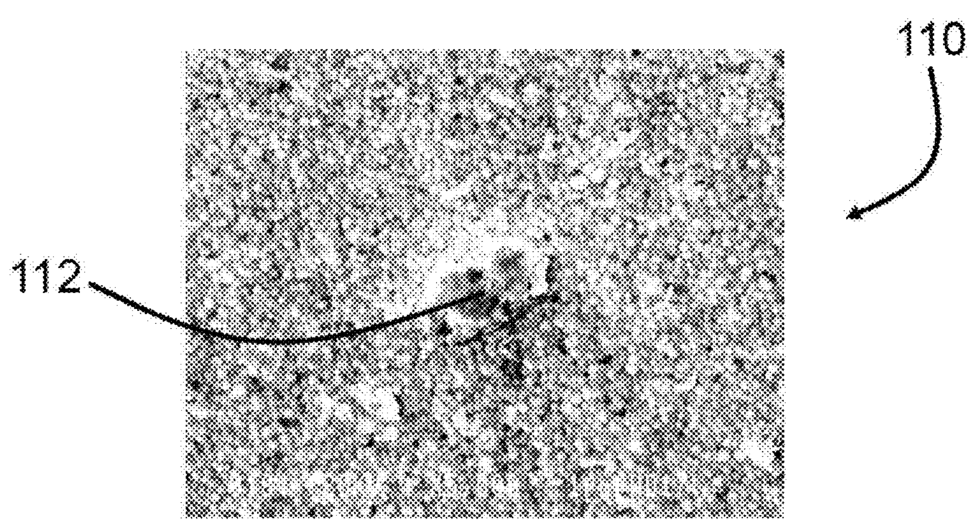
(57) **ABSTRACT**

A method of manufacturing ceramic tape includes a step of directing a tape of partially-sintered ceramic into a furnace. The tape is partially-sintered such that grains of the ceramic are fused to one another yet the tape still includes at least 10% porosity by volume, where the porosity refers to volume of the tape unoccupied by the ceramic. The method further includes steps of conveying the tape through the furnace and further sintering the tape as the tape is conveyed through the furnace. The porosity of the tape decreases during the further sintering step.



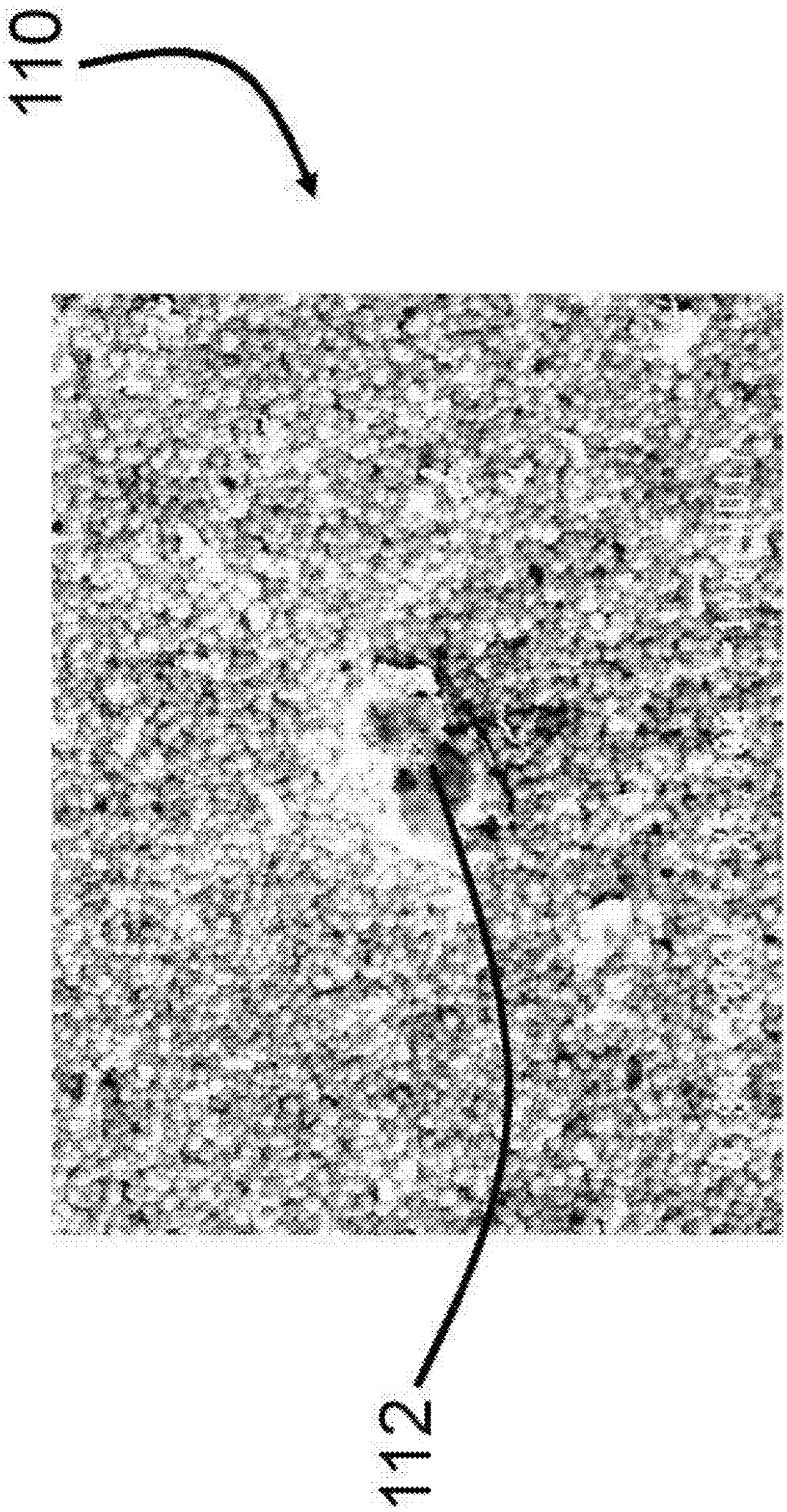
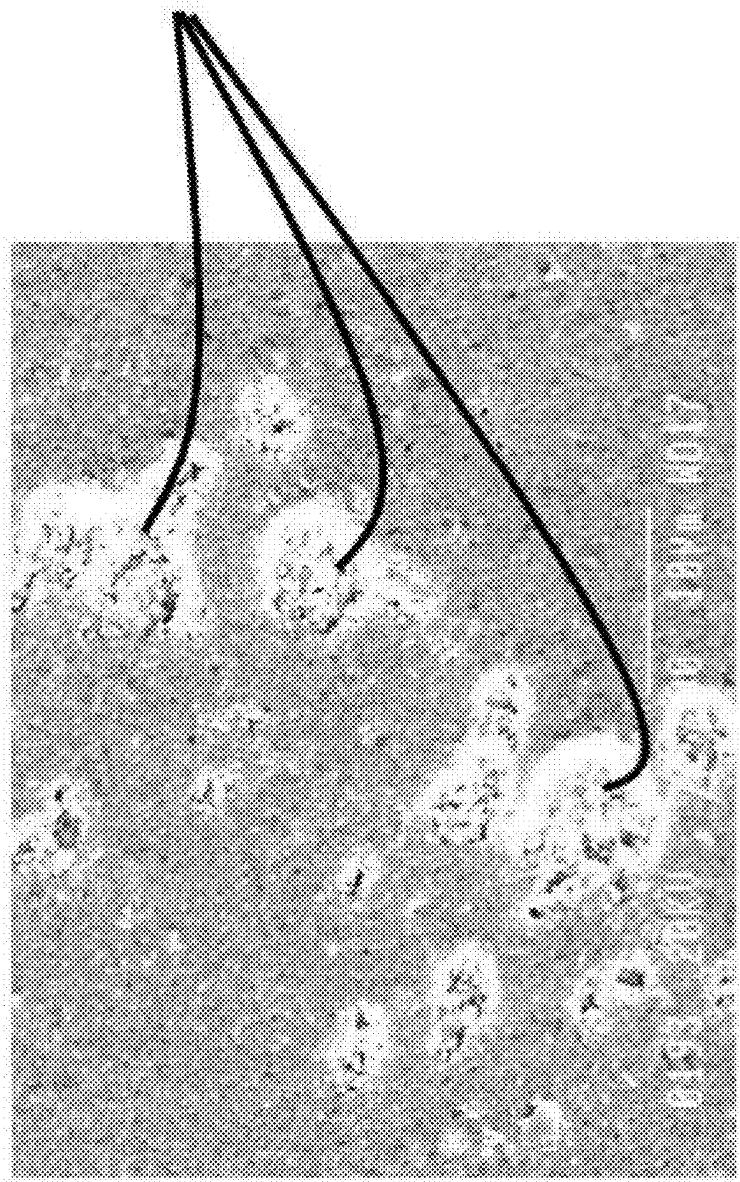


FIG. 1

212



210

FIG. 2

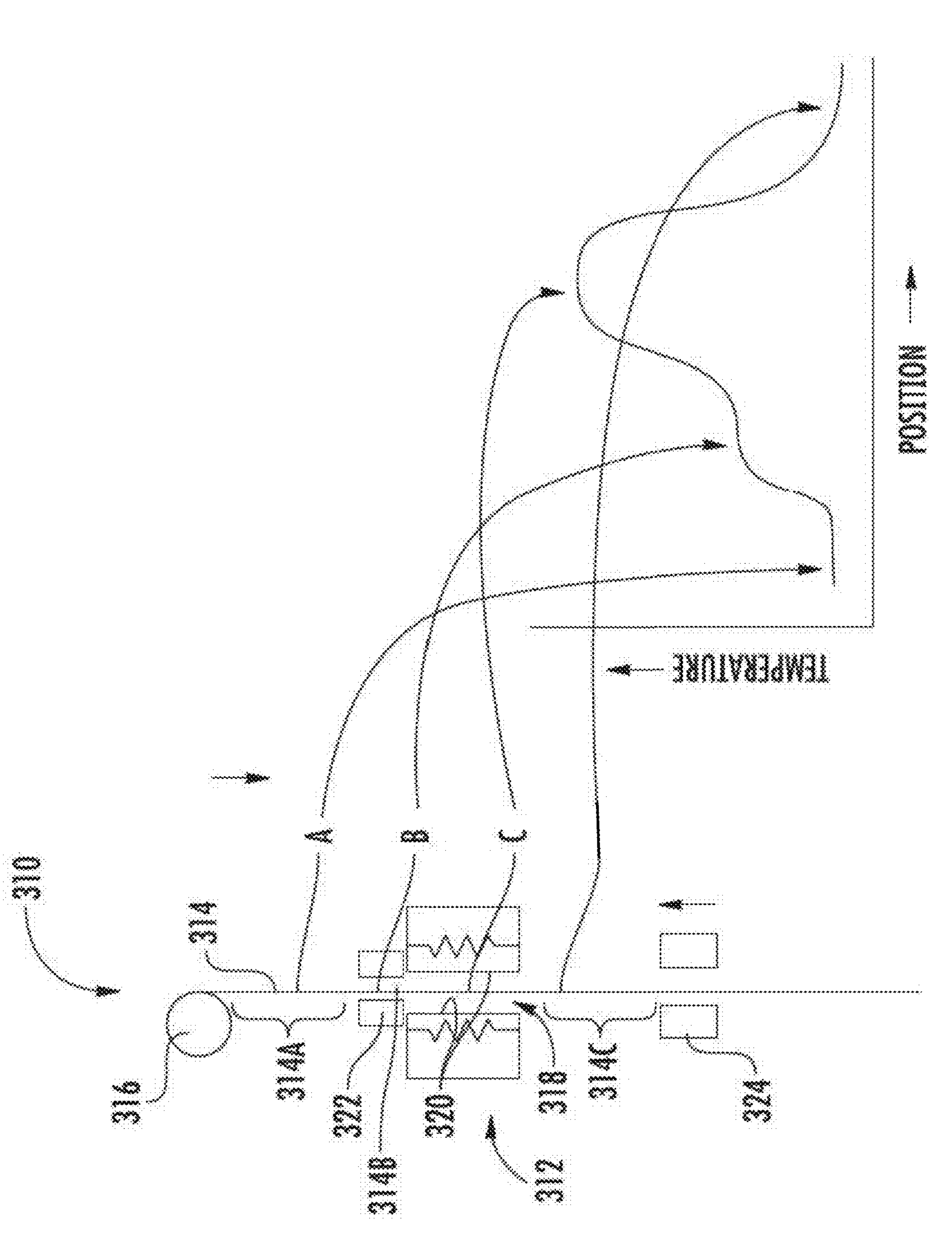

310
314
316
314A
322
314B
320
312
318
314C
324
A
B
C
TEMPERATURE
POSITION

FIG. 3A

FIG. 3B

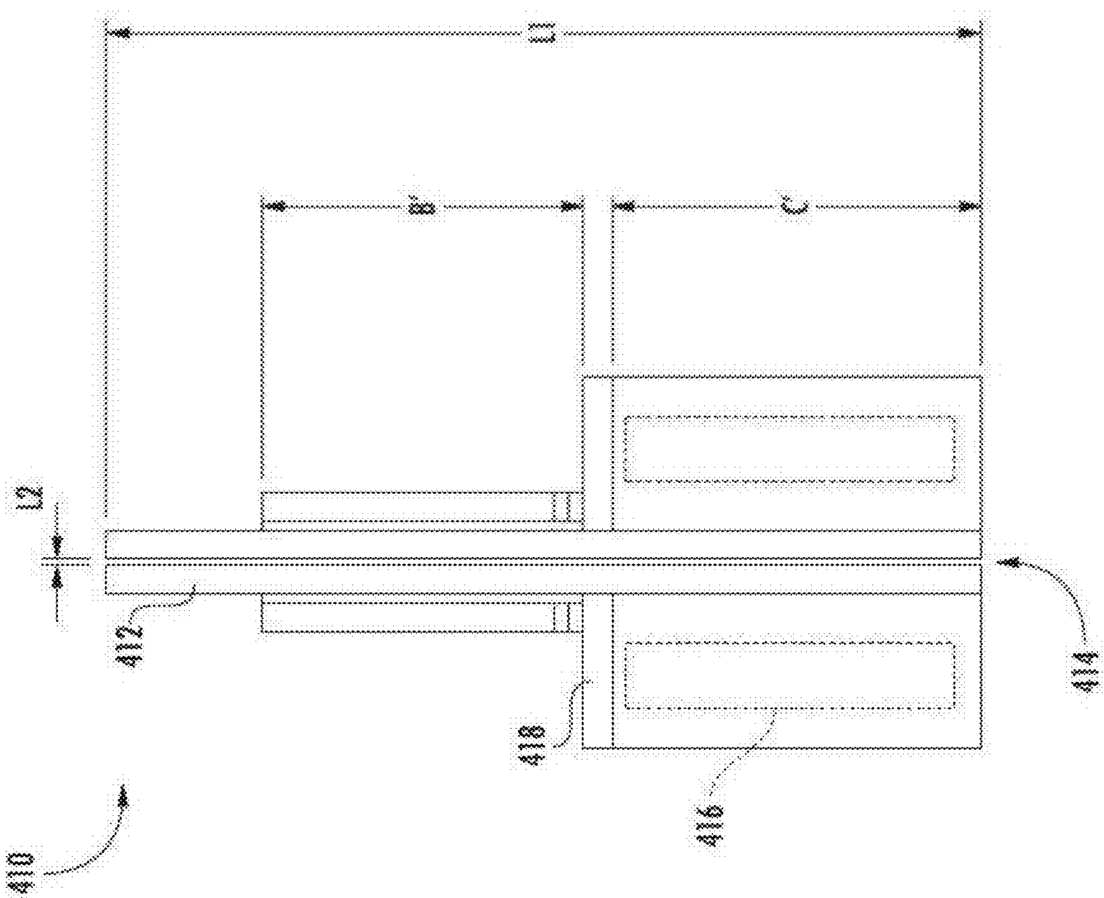


FIG. 4

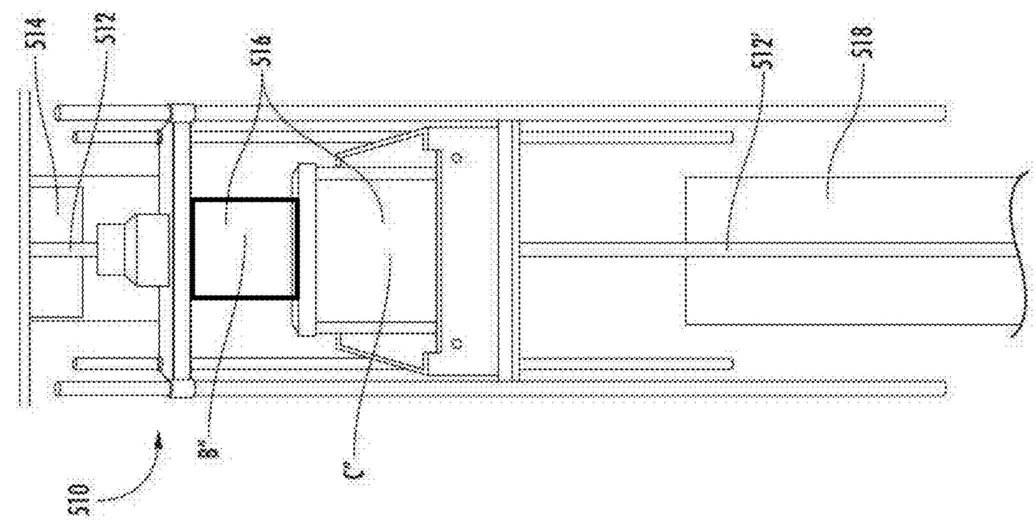


FIG. 5

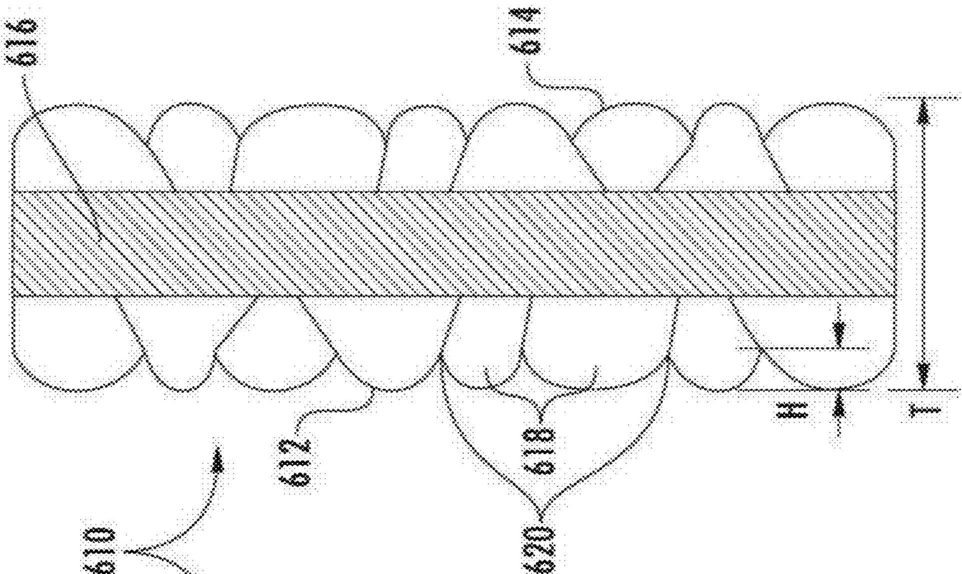


FIG. 6B

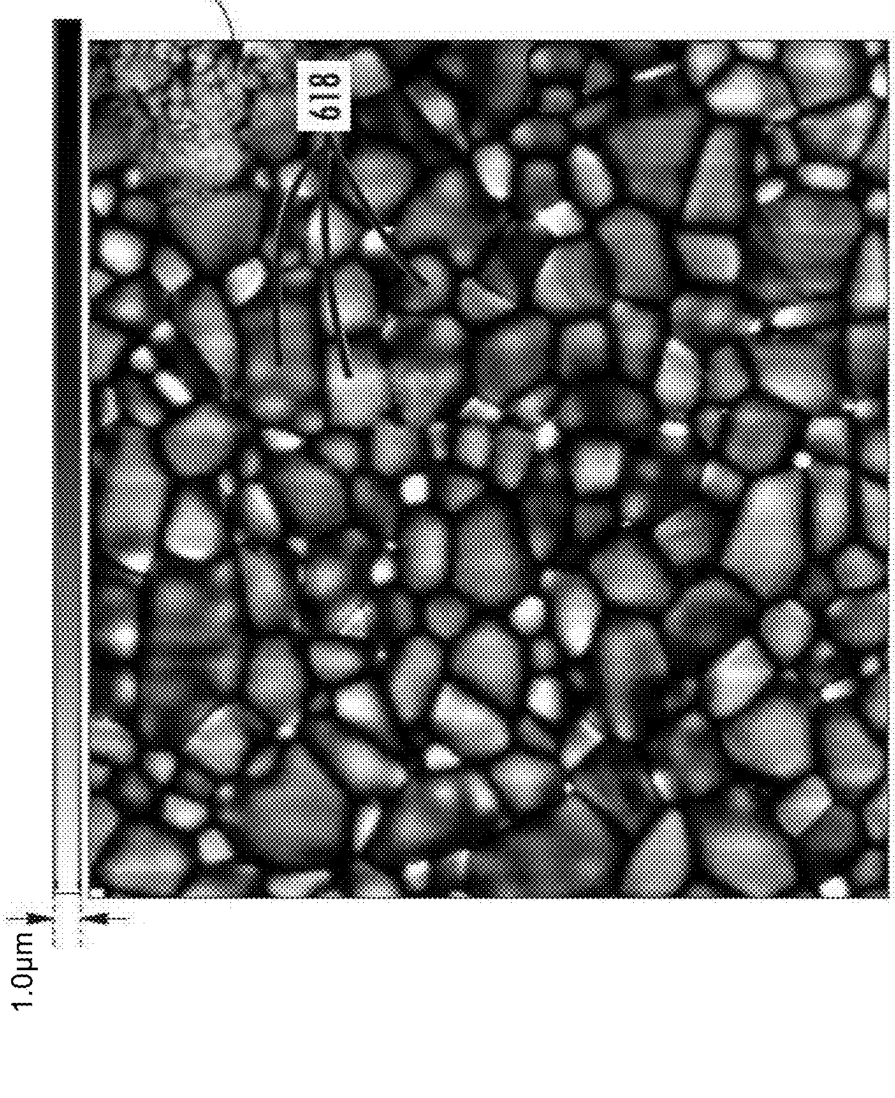


FIG. 6A

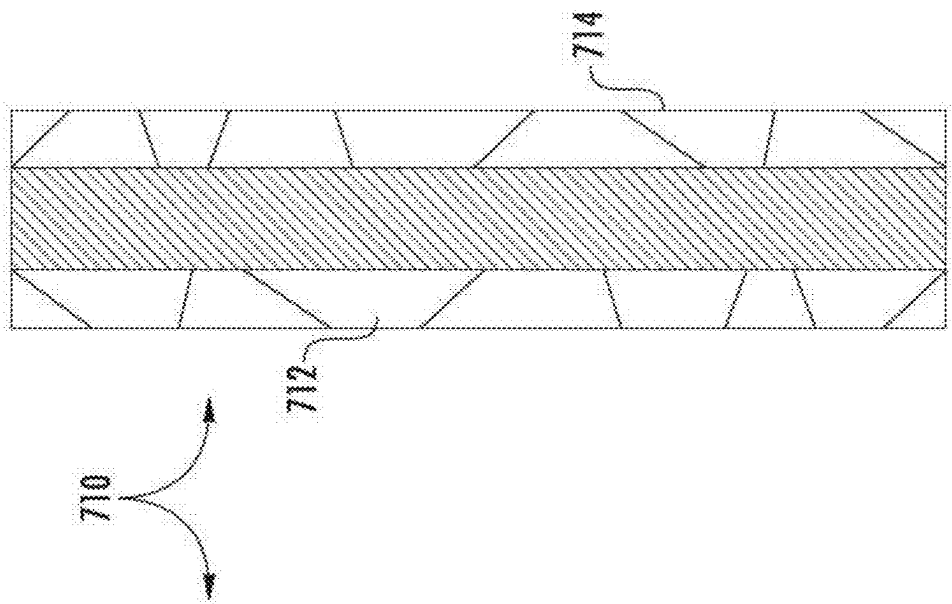


FIG. 7B

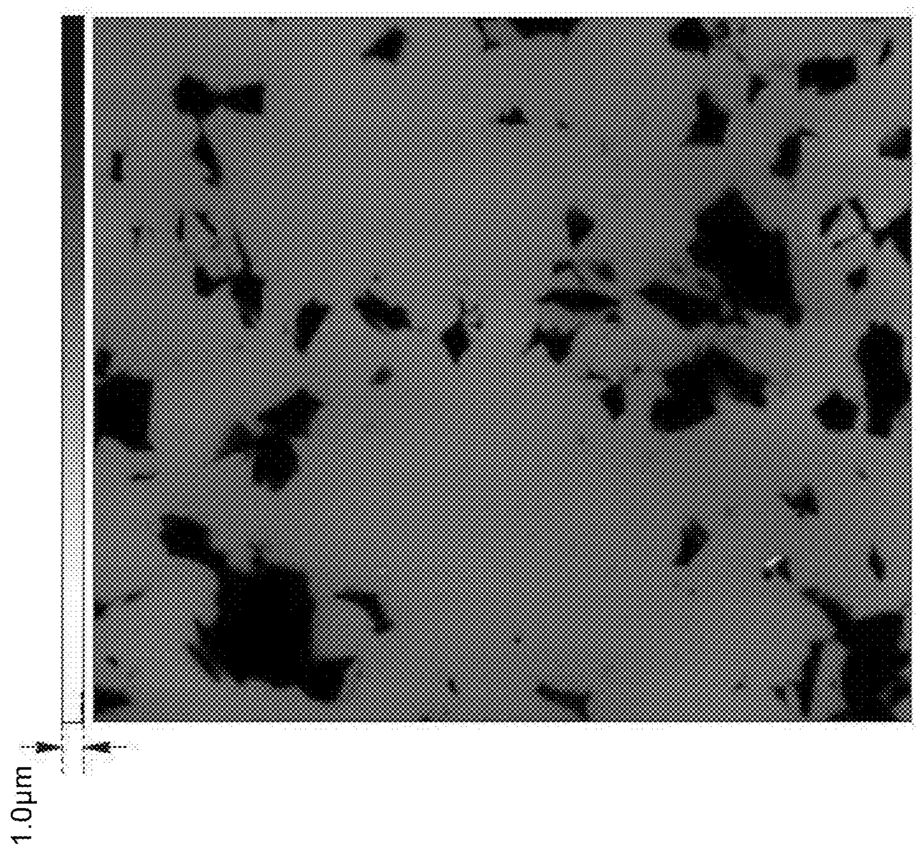


FIG. 7A

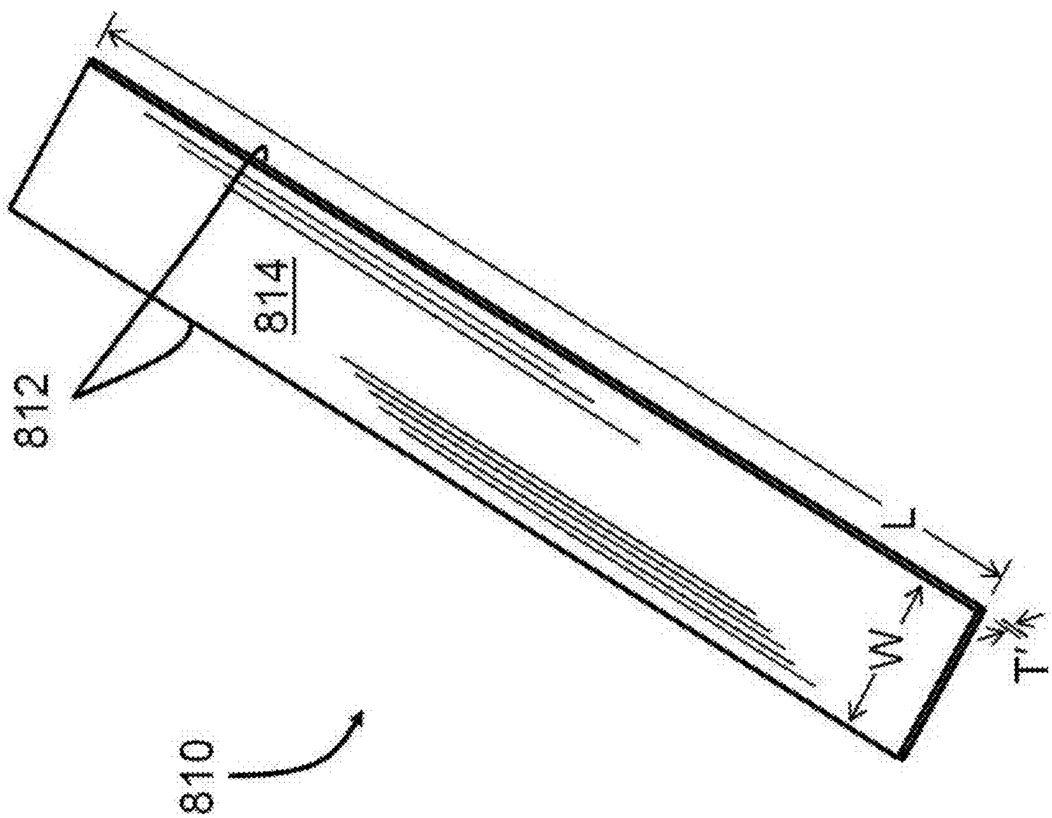


FIG. 8

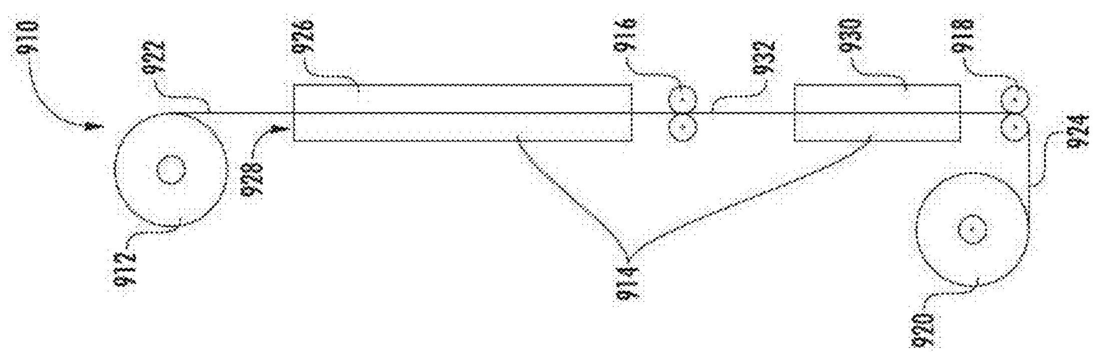


FIG. 9

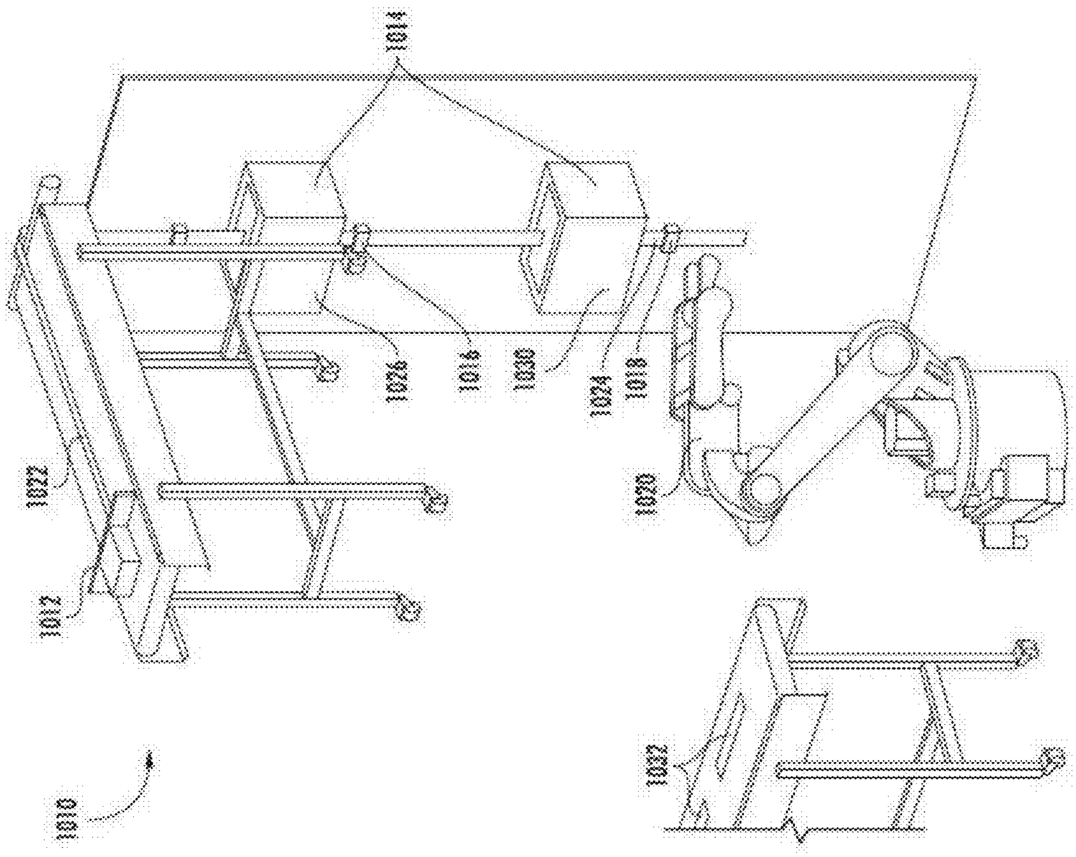
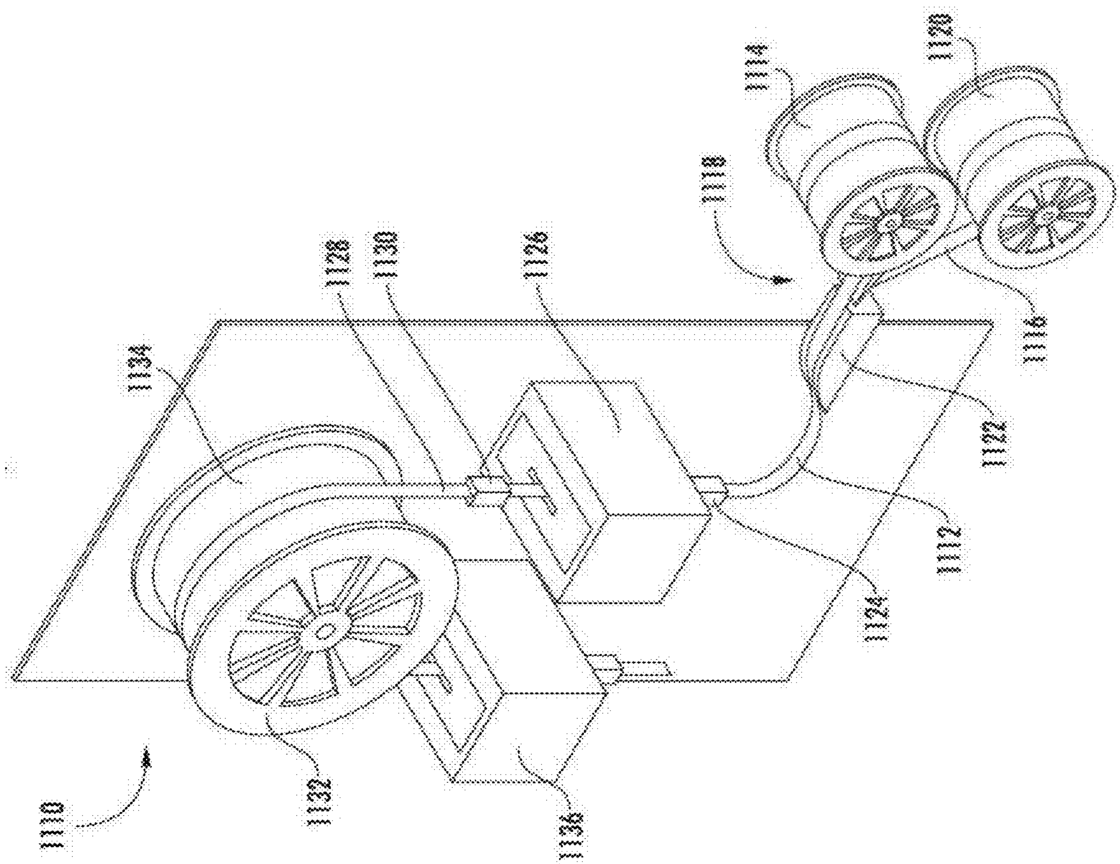


FIG 10


1110
1132
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1126
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1120
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1112
1124

FIG. 11

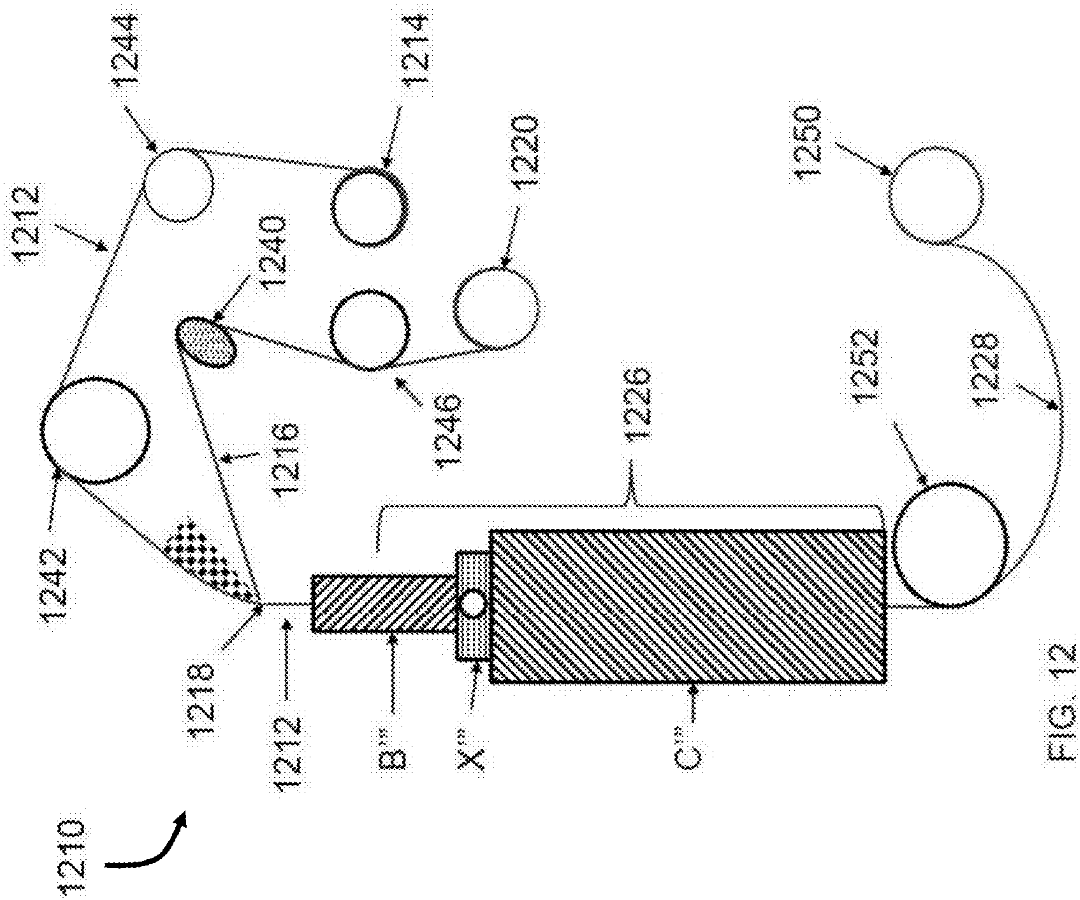

1210
1212
1244
1214
1220
1240
1242
1216
1246
1226
1250
1252
1228
1218
1212
B'''
X'''
C'''

FIG. 12

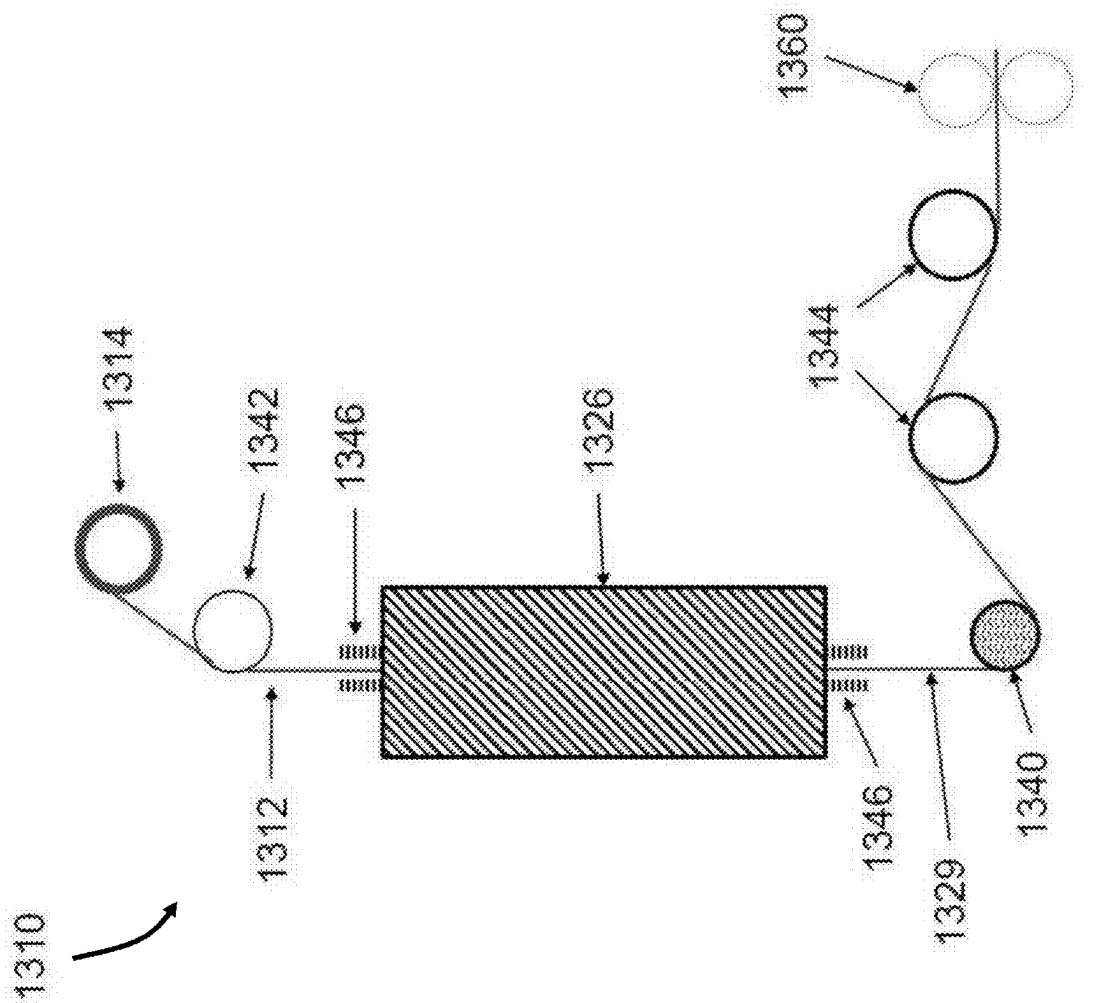


FIG. 13

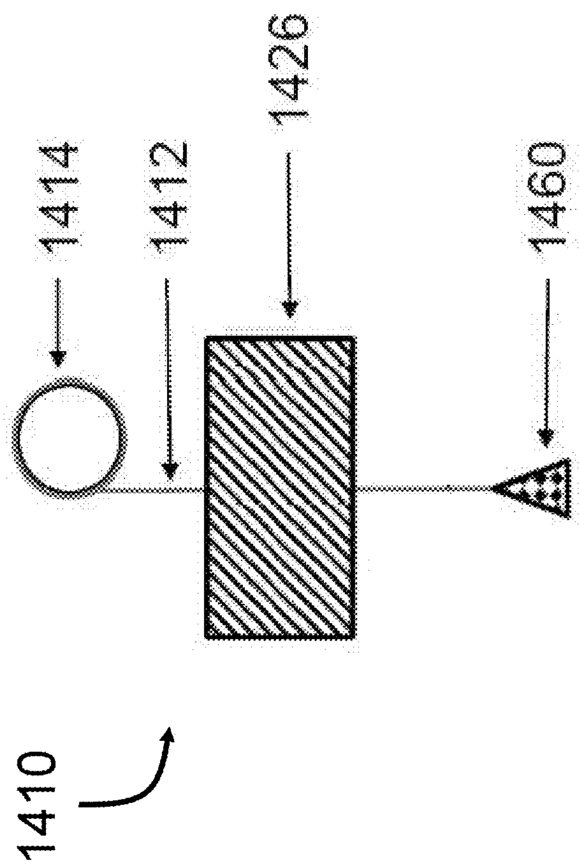


FIG. 14

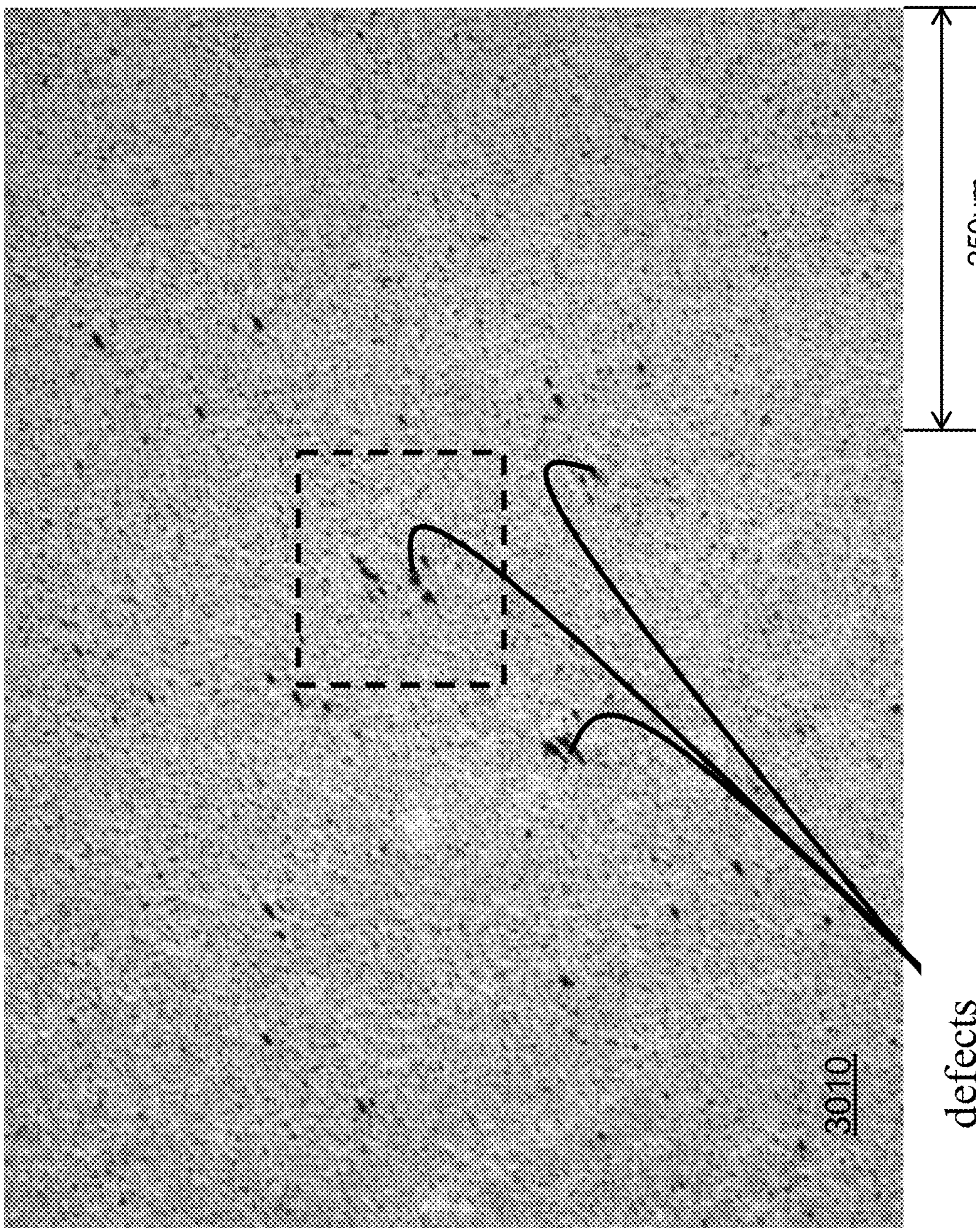


FIG. 15

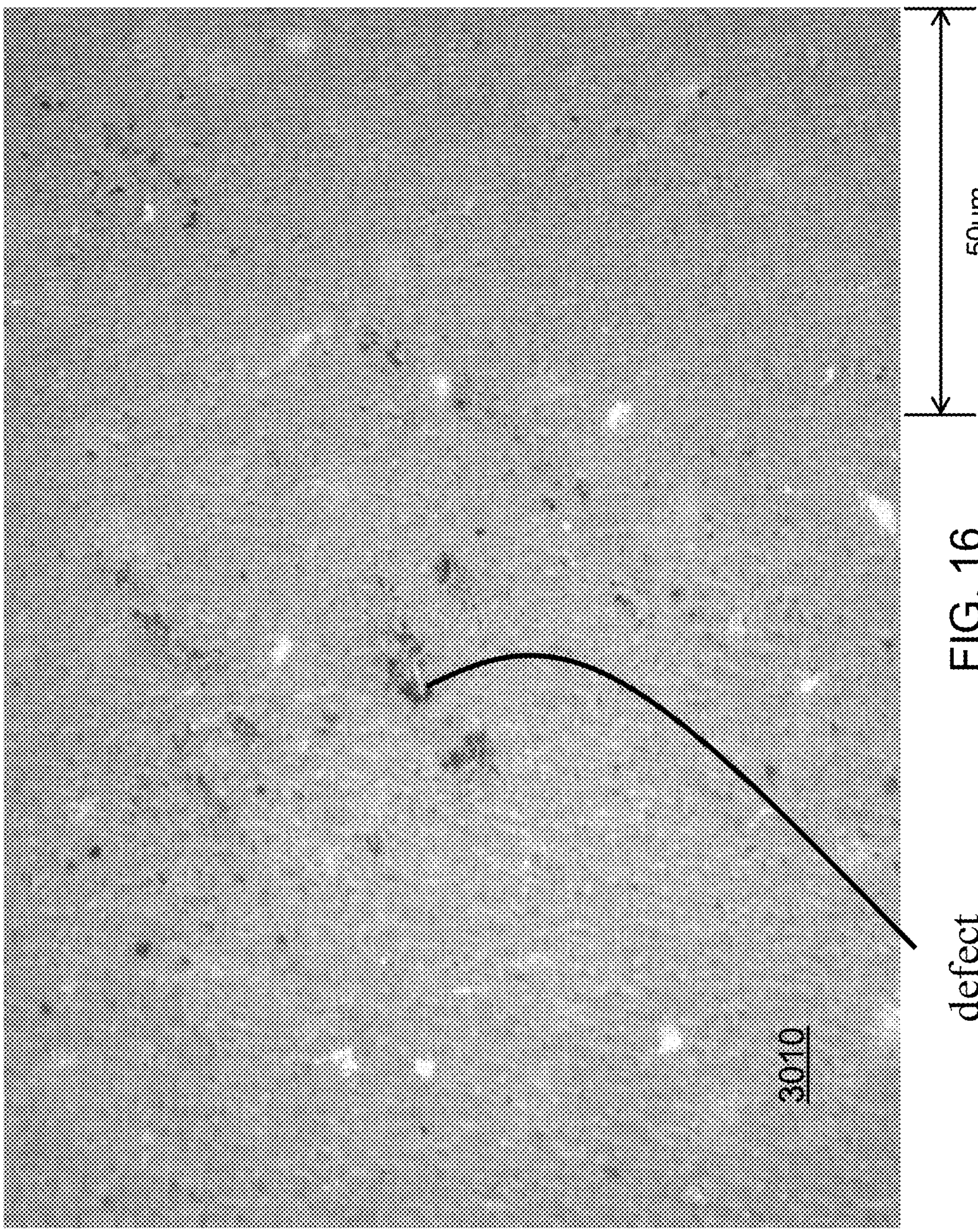
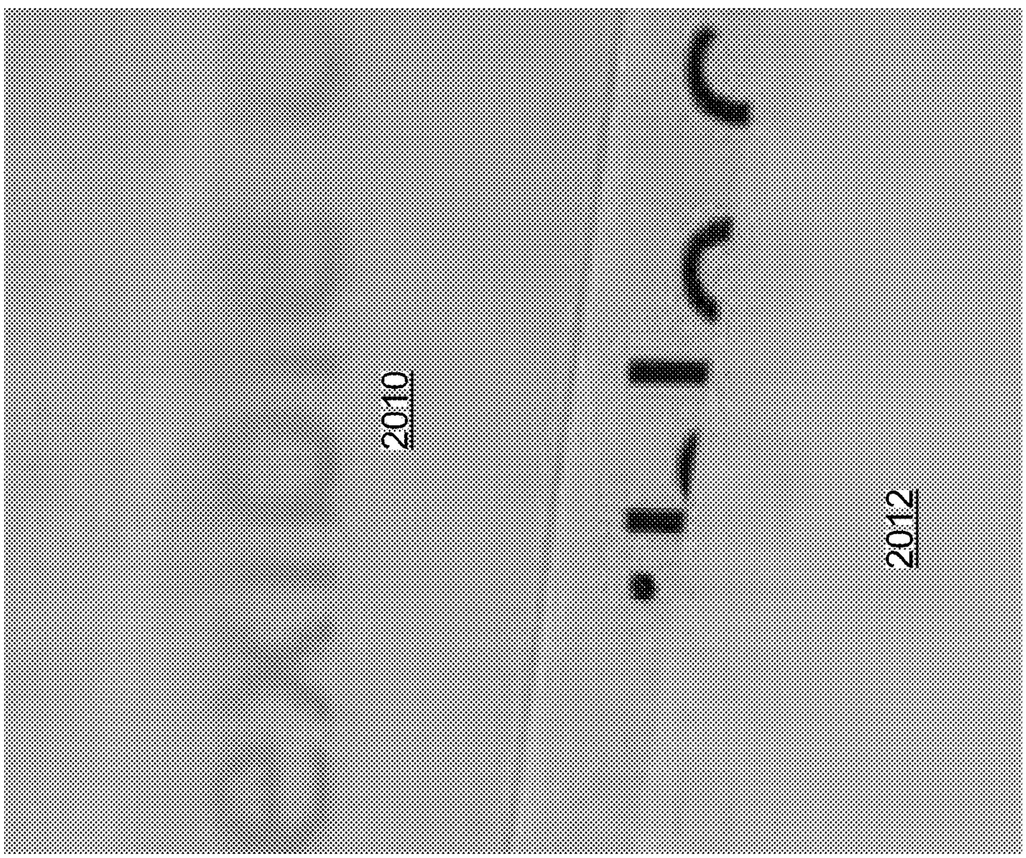


FIG. 16

FIG. 17



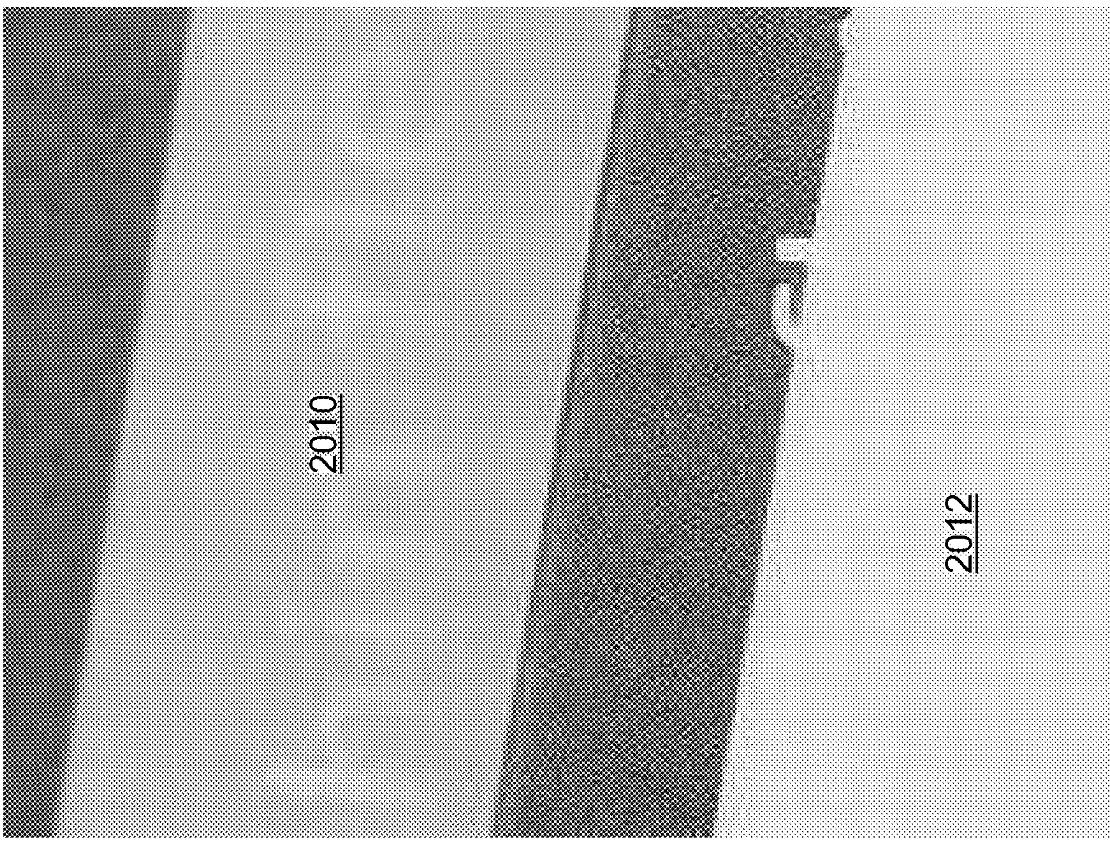


FIG. 18

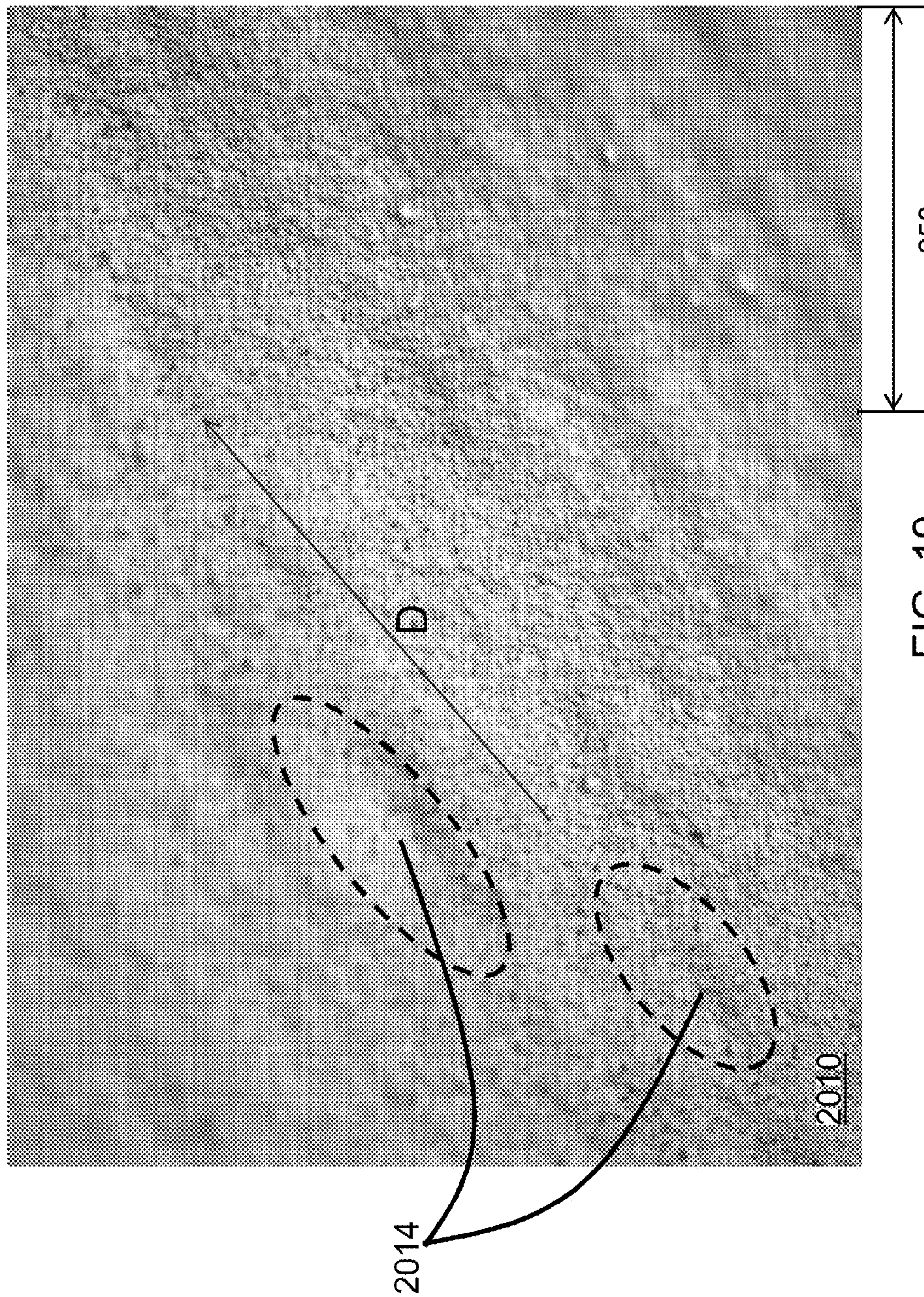


FIG. 19

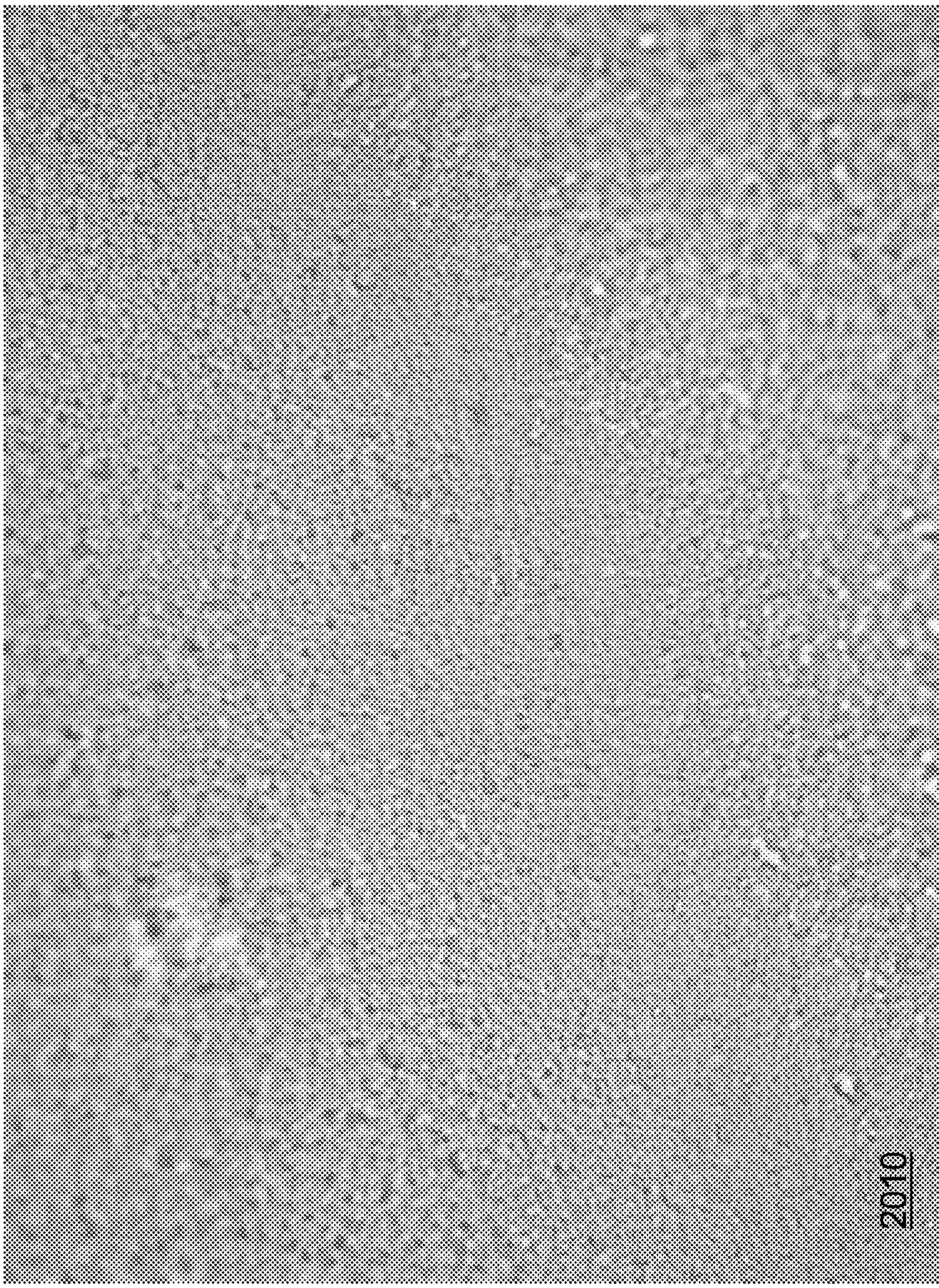


FIG. 20

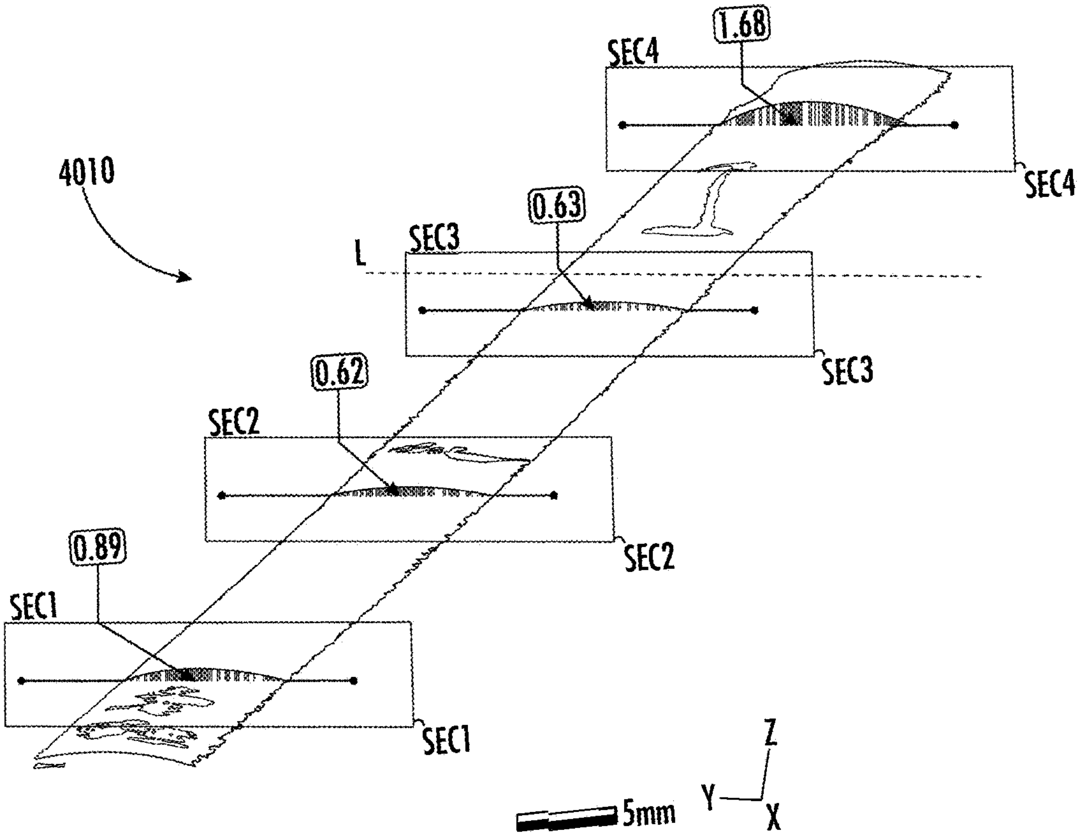

1.68
SEC4
SEC4
4010
0.63
SEC3
L
SEC3
0.62
SEC2
SEC2
0.89
SEC1
SEC1
5mm
Z
Y
X

FIG. 21

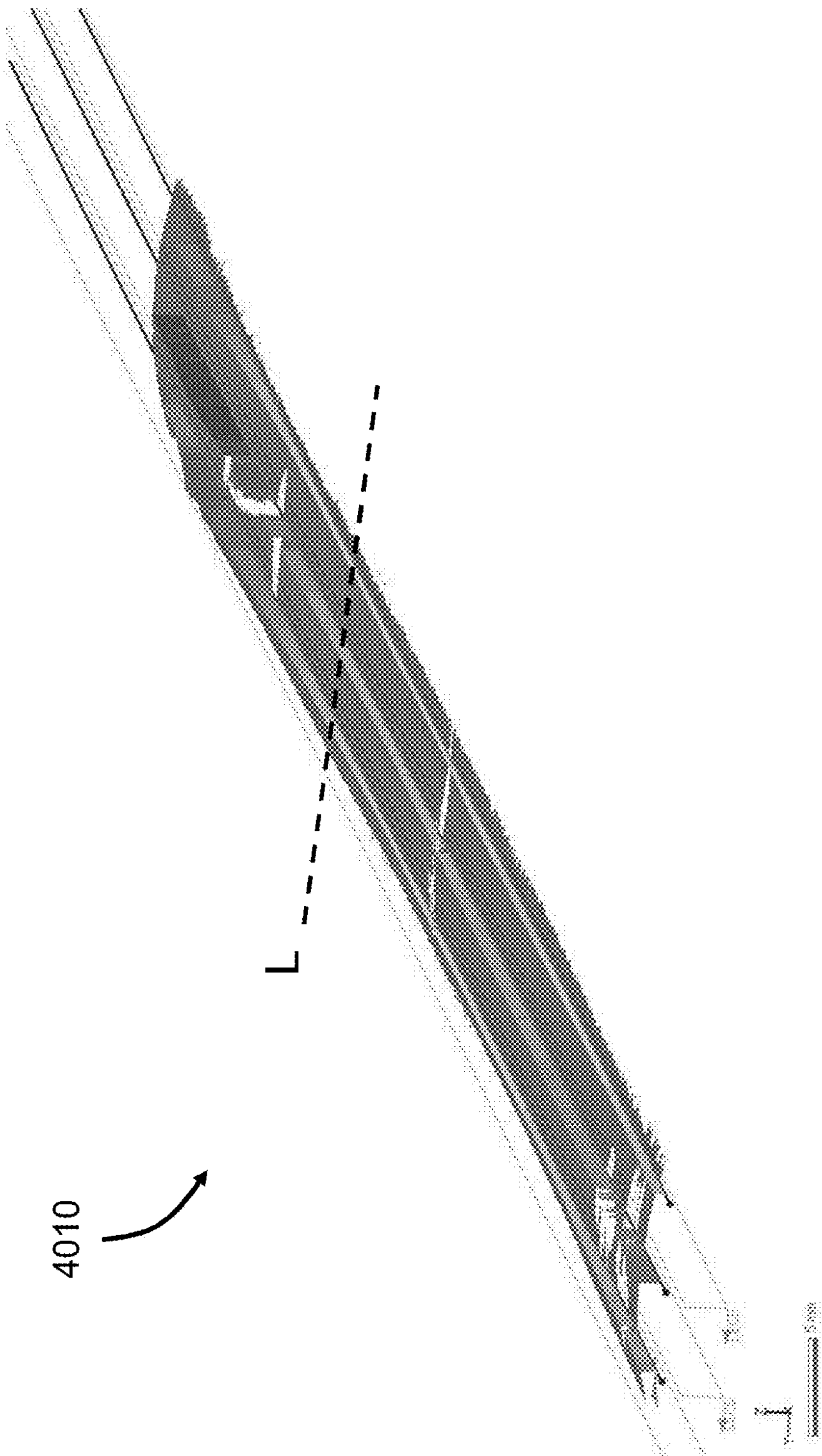


FIG. 22

MANUFACTURING LINE, PROCESS, AND SINTERED ARTICLE

PRIORITY

[0001] This Application is a continuation of U.S. application Ser. No. 18/588,354 filed on Feb. 27, 2024, which is a continuation of U.S. application Ser. No. 18/239,211 filed Aug. 29, 2023 and issued Apr. 9, 2024 as U.S. Pat. No. 11,953,264, which is a continuation of U.S. application Ser. No. 18/115,852 filed Mar. 1, 2023 and issued Sep. 26, 2023 as U.S. Pat. No. 11,768,032, which is a continuation of U.S. application Ser. No. 17/468,752 filed Sep. 8, 2021 and issued Apr. 18, 2023 as U.S. Pat. No. 11,629,915, which is a continuation of U.S. application Ser. No. 17/173,637 filed Feb. 11, 2021 and issued on Oct. 19, 2021 as U.S. Pat. No. 11,148,321, which is a continuation of U.S. application Ser. No. 17/076,044 filed Oct. 21, 2020 and issued on Apr. 6, 2021 as U.S. Pat. No. 10,967,539, which is a continuation of U.S. application Ser. No. 16/930,724 filed Jul. 16, 2020 and issued Dec. 29, 2020 as U.S. Pat. No. 10,875,212, which is a continuation of U.S. application Ser. No. 15/218,689 filed Jul. 25, 2016 and issued on Sep. 8, 2020 as U.S. Pat. No. 10,766,165, which is a continuation of International Application No. PCT/US2016/039708 filed Jun. 28, 2016, which claims the priority benefit of U.S. Application No. 62/185, 950 filed Jun. 29, 2015, each of which is hereby incorporated by reference herein in its entirety.

BACKGROUND

[0002] Aspects of the present disclosure generally relate to processes for sintering green tape, such as green tape including polycrystalline ceramic grains bound in an organic binder, as well as sintered articles, such as ceramic sheets or tapes made from such processes.

[0003] Articles, such as thin sheets, tapes, or ribbons of ceramic have many potential uses, such as serving as waveguides, when the ceramic is transmissive to light, serving as substrates that may be coated or laminated, and integrated in batteries and other components, or other applications. Such articles may be manufactured by forming large ingots of the sintered material, cutting slivers or plates of the material, and polishing the corresponding articles to a desired form and surface quality. Polishing helps to remove flaws or defects on the surfaces of the articles, but is time-and resource-consuming.

[0004] Such articles may also be manufactured by tape casting, gel casting, or other processes that include sintering of green tapes, such as strips of inorganic grains bound in an organic binder. The green tapes are typically placed upon a surface, called a setter board, and placed inside a furnace that burns off the organic binder and sinters the inorganic grains. The setter board is typically formed from a refractory material that can withstand the sintering process. The setter board supports the tape when the binder is removed.

[0005] Applicants have observed that sintering causes a green tape to contract, dragging portions of itself across the setter board during the contraction. A result is that the supported side of the resulting sintered article has surface defects, such as drag grooves, sintered debris, impurity patches, etc. transferred from refractory material of the setter board to the sintering article. FIGS. **1** and **2** show examples of surface defects **112**, **212** on sintered ceramic articles **110**, **210**, such as defects caused by a setter board during sintering. Applicants believe that these defects diminish the strength of the respective article by providing sites for stress concentrations and crack initiations.

[0006] Additionally, when manufacturing thinner and thinner sintered articles (e.g., sheets, tapes, ribbons), Applicants postulate that at some point, the sintered articles may become so thin that they are difficult if not impossible to polish. Accordingly, for such articles, those of ordinary skill in the art may be unable to remove surface defects induced by setter boards during sintering or defects caused by cutting. Similarly, for thicker, yet still thin sintered articles, Applicants postulate that at some point the articles have too much surface area to polish. Control of conventional polishing equipment with fragile and/or thin sheets of large surface area may become unwieldy and/or impractical. Accordingly, thin articles, particularly those with relatively large surfaces areas, having qualities generally associated with polishing, such as flatness, smoothness, and/or defect-free surfaces, may be unattainable using conventional manufacturing methods and/or those of ordinary skill in the art may avoid trying to manufacturing such articles due to strong disincentives in terms of overcoming manufacturing challenges and associated costs per article.

[0007] A need exists for equipment and manufacturing processes for making articles, such as tapes and sheets of polycrystalline ceramics, metals, or other materials that may be sintered, where the articles may be efficiently manufactured, such as without excessive polishing, while also having good mechanical properties, such as due to having few surface defects. Such articles may be useful as substrates such as in batteries, on printed circuit boards, as cover sheets for displays, such for handheld devices, or the articles may be otherwise useful.

SUMMARY

[0008] Applicants have discovered technology that removes the setter board from the process of sintering green tape, where resulting sintered articles may be unpolished, yet may have good mechanical properties. In some embodiments, technology disclosed herein relates to a continuous manufacturing line, where a continuous tape includes a green section including inorganic particles held by an organic binder. On the manufacturing line, the green section is directed to a first heated location to burn off or char the binder, forming an unbound section of the same tape. Next, along the manufacturing line, the unbound section is run through a second heated location for at least partial sintering of the inorganic particles. The first and second heated locations may be heated by the same or different furnaces on the manufacturing line. Additional heated locations may be on the manufacturing line to further process the tape, such as a third heated location for completing the sintering of the tape, if the tape is only partially sintered at the second heated location. Partial sintering at the second heated location may allow the tape to be tensioned for further sintering at the third heating location, where the tension holds the tape flat, thereby facilitating a particularly flat sintered sheet and/or one with few sintering-induced surface defects.

[0009] The above is in part achieved by orienting the green tape past the second heated location in a manner that does not require setter board support for the green tape, such as vertically orienting the tape. Surprisingly, Applicant have found that the weight of the tape below the unbound section need not necessarily sever or pull apart the tape at the unbound section before the at least partial sintering occurs, despite the binder of the tape being burned off or charred. Applicants discovered that the tape is able to hold itself together long enough for at least partial sintering, without a setter board. As a result, the sintered article is free of contact-induced surface defects produced during sintering typically caused by setter boards. Surfaces on both sides of the sintered article are consistent with one another in terms of number of defects, and that number is low enough that the resulting sintered article may have improved mechanical properties, such as increased tensile strength, relative to articles with more surface defects.

[0010] Additional features and advantages are set forth in the Detailed Description that follows, and in part will be readily apparent to those skilled in the art from the description or recognized by practicing the embodiments as described in the written description and claims hereof, as well as the appended drawings. It is to be understood that both the foregoing general description and the following Detailed Description are merely exemplary, and are intended to provide an overview or framework to understand the nature and character of the claims.

BRIEF DESCRIPTION OF THE FIGURES

[0011] The accompanying Figures are included to provide a further understanding, and are incorporated in and constitute a part of this specification. The drawings illustrate one or more embodiments, and together with the Detailed Description serve to explain principles and operations of the various embodiments. As such, the disclosure will become more fully understood from the following Detailed Description, taken in conjunction with the accompanying Figures, in which:

[0012] FIGS. **1** and **2** are digital images of ceramic material with surface defects.

[0013] FIG. **3**A is a schematic diagram of a manufacturing line according to an exemplary embodiment.

[0014] FIG. **3**B is a plot conceptually showing temperature versus position along the manufacturing line of FIG. **3**A.

[0015] FIG. **4** is a cross-sectional view of a furnace according to an exemplary embodiment.

[0016] FIG. **5** is a digital image of a manufacturing line according to an exemplary embodiment with tape being processed.

[0017] FIG. **6**A is a digital image of an unpolished surface of a sintered ceramic.

[0018] FIG. **6**B is a conceptual side profile of unpolished sintered ceramic.

[0019] FIG. **7**A is a digital image of a polished surface of a sintered ceramic.

[0020] FIG. **7**B is a conceptual side profile of polished sintered ceramic.

[0021] FIG. **8** is a perspective view of a sintered article in the form of a thin sintered tape of material, according to an exemplary embodiment.

[0022] FIG. **9** is a schematic diagram from a side view of a manufacturing line according to another exemplary embodiment.

[0023] FIGS. **10-11** are perspective views of manufacturing lines according to other exemplary embodiments.

[0024] FIG. **12** is a schematic diagram of a manufacturing line, or a portion thereof, according to an exemplary embodiment.

[0025] FIG. **13** is a schematic diagram of a manufacturing line, or a portion thereof, according to another exemplary embodiment.

[0026] FIG. **14** is a schematic diagram of a manufacturing line, or a portion thereof, according to yet another exemplary embodiment.

[0027] FIG. **15** is a micrograph of a thin ceramic sheet sintered on a setter board at 100 times magnification.

[0028] FIG. **16** is the same sheet as FIG. **15** at 500 times magnification, generally from within the dashed box shown in FIG. **15**.

[0029] FIG. **17** compares partially and fully sintered tapes, made using inventive processes disclosed herein, overlaying dark lettering on white paper.

[0030] FIG. **18** compares partially and fully sintered tapes, made using inventive processes disclosed herein, overlaying white lettering on dark paper.

[0031] FIG. **19** is a micrograph of a thin ceramic sheet sintered using inventive processes disclosed herein at 100 times magnification.

[0032] FIG. **20** is the same sheet as FIG. **19** at 500 times magnification.

[0033] FIGS. **21-22** are surface scans of a tape according to an exemplary embodiment, with widthwise (FIG. **21**) and lengthwise (FIG. **22**) height profiles.

DETAILED DESCRIPTION

[0034] Before turning to the following Detailed Description and Figures, which illustrate exemplary embodiments in detail, it should be understood that the present inventive technology is not limited to the details or methodology set forth in the Detailed Description or illustrated in the Figures. For example, as will be understood by those of ordinary skill in the art, features and attributes associated with embodiments shown in one of the Figures or described in the text relating to one of the embodiments may well be applied to other embodiments shown in another of the Figures or described elsewhere in the text.

[0035] Referring to FIGS. **3**A-**3**B, a manufacturing line **310** includes a furnace system **312** and a workpiece (e.g., ribbon, tape, web, line, material), such as a tape **314**, shown from a side view, extending into the furnace system **312**. The tape **314** may be routed around a curve or roller **316** and directed toward the furnace system **312**. According to an exemplary embodiment, the furnace system **312** includes a passage **318**, which includes a binder burn-off location B and/or a sintering location C for at least partially sintering the tape **314** after the tape has passed the binder burn-off location B. In some embodiments, the binder burn-off location B is adjacent to the sintering location C, such as directly above or below the sintering location C along the manufacturing line **310**, such as within 1 meter, within 50 centimeters, within 10 centimeters. As will be discussed further, close placement of the binder burn-off location B and the sintering location C reduces the time/length that the tape **314** is unbound by binder prior to sintering.

[0036] According to an exemplary embodiment, the passage **318** of the furnace system **312** is oriented so that the tape **314** may extend generally vertically through the passage **318**, such as without contacting surfaces **320** of at least sections of the furnace system **312** directed to burning off binder (e.g., binder burn-off location B) and/or at least partially sintering the tape **314** (e.g., sintering location C). For example, the passage **318** may be oriented so that the tape **314** may extend generally vertically, and move upward and/or downward along a path that is oriented between 45 and 135 degrees relative to horizontal, such as between 60 and 120 degrees, such as at 90 degrees plus or minus 10 degrees. Passing the tape **314** through the binder burn-off location B and/or a sintering location C, without contacting the tape **314** with surfaces **320** of the sintering location C and/or surfaces **322** of the binder burn-off location B, is believed to improve the surface quality of the tape **314** as it is processed by the furnace system **312**, by reducing material transfer and/or scoring or otherwise shaping of the tape **314** via contact.

[0037] According to an exemplary embodiment, a first section of the tape **314** is a green tape section **314**A, which may be positioned at a location A along the manufacturing line **310**. According to an exemplary embodiment, the green tape section **314**A includes polycrystalline ceramic and/or minerals (e.g., alumina, zirconia, lithium garnet, spinel) bound by an organic binder (e.g., polyvinyl butyral, dibutyl phthalate, polyalkyl carbonate, acrylic polymers, polyesters, silicones, etc.). In contemplated embodiments, the green tape section **314**A may include metal particles bound in an organic binder. In other contemplated embodiments, the green tape section **314**A may include glass grains (e.g., high purity silica grains, borosilicate, aluminosilicate, soda lime) or other inorganic grains bound by an organic binder. In contemplated embodiments, the green tape section **314**A may include glass-ceramic particles (e.g. cordierite, LAS lithium aluminosilicates, Nasicon structure lithium metal phosphates, celsian) bound in an organic binder. According to an exemplary embodiment, the green tape section **314**A has a porosity of from about 0.01 to about 25 vol % and/or the inorganic particles have a median particle size diameter of from 50 to 1,000 nanometers and a Brunauer, Emmett and Teller (BET) surface area of from 2 to 30 m^2/g. In other contemplated embodiments, the above materials may be bound by inorganic binders or other binders and/or the above materials may be otherwise sized or have other porosity.

[0038] As the green tape section **314**A passes the binder burn-off location B, the furnace system **312** is configured to burn off and/or char, due to oxidation, volatilization, and/or cross-link, binder material from the green tape section **314**A, such as most of the binder, such as at least 90% of the binder. According to an exemplary embodiment, the green tape section **314**A is self-supported through the burn-off location B and need not and/or does not contact surfaces **322** of the burn-off location B.

[0039] Beyond the binder burn-off location B, the tape **314** is no longer "green" and a second section of the tape **314** is a unbound tape section **314**B (e.g., burned-off tape section, charred binder tape section), which may be unsintered, yet may be without binder or with charred binder. Because the unbound tape section **314**B is without working and/or uncharred binder, one of ordinary skill in the art may expect the unbound tape section **314**B to simply collapse or fall apart under its own weight or weight of portions of the tape **314** below the unbound tape section **314**B, such as due to lack of binder. However Applicants have discovered that the unbound tape section **314**B may remain intact, despite the binder being burned off and/or charred, if the tape **314** is properly handled, such as if tension on the tape **314** is controlled and/or if the tape **314** is not bent and/or reoriented prior to at least partial sintering of inorganic material (e.g. ceramic grains) of the tape **314**.

[0040] Referring still to FIG. **3**A, the unbound tape section **314**B portion of the tape **314** then passes into and/or by the sintering location C, and the furnace system **312** is configured to at least partially sinter the polycrystalline ceramic or other inorganic material of the unbound tape section **314**B. For example, polycrystalline ceramic grains may be sintered such that the grains bond or fuse to one another yet the tape **314** still includes a large amount of porosity (e.g., at least 10% by volume, at least 30% by volume), where the "porosity" refers to the portions of the volume of the tape unoccupied by the inorganic material, such as the polycrystalline ceramic.

[0041] Once at least partially sintered, the corresponding section of the tape **314** is an at least partially sintered tape section **314**C. Partially and not fully sintering the at least partially sintered tape section **314**C may increase the strength of the tape **314** to the extent that tension may be applied to the tape **314** to facilitate subsequent shaping of the tape **314**. According to an exemplary embodiment, under tension, additional sintering of the tape **314** occurs to produce a particularly flat or otherwise-shaped sintered article (see generally FIG. **5**).

[0042] According to an exemplary embodiment, the manufacturing line **310** further includes a tension regulator **324**, which influences tension in the tape **314**, such as by directly interacting with the at least partially sintered tape section **314**C. The tension regulator **324** may control and separate tension in the tape **314** above versus below the tension regulator **324** such that tension may be different in the portions of the tape **314** on either side of the tension regulator **324**. In some embodiments, the tension regulator **324** includes an air bearing, where air may be directed with or against a direction that the tape **314** moves through the manufacturing line **310**, such as to adjust tension in the tape **314**. In other embodiments, the tension regulator **324** includes nip rollers that pull or push the tape **314** to influence tension in the tape **314**. In still other embodiments, the tension regulator **324** may be a wheel (sec, e.g., FIG. **12**), where friction on a surface of the wheel as well as rotation of the wheel influences tension in the tape **314**. As discussed, tension in the tape **314** may be used to shape the tape **314** as the tape **314** is sintered, such as at the sintering location C or elsewhere along the manufacturing line **310**. Additionally, tension (positive or negative amounts thereof) applied to the tape **314** by the tension regulator **324** may help hold the unbound tape section **314**B together, by influencing the tension in that section.

[0043] Referring now to FIG. **3**B, temperatures of the tape **314** may vary along the length of the tape **314** as a function of position of the particular portion of the tape **314** along the manufacturing line **310**. The green tape section **314**A, prior to entering the binder burn-off location B may experience a first temperature, such as room temperature (e.g., about 25° C.). Near the binder burn-off location B, the temperature experienced by the unbound tape section **314**B of the tape **314** may be greater than that experienced by the green tape section **314**A, such as at least 200° C., at least 400° C. Near and at the sintering location C, the temperature experienced by the tape **314** may be greater still than that experienced by the tape **314** near the binder burn-off location B, such as at least 800° C., at least 1000° C. at the sintering location C. Portions of the tape **314** located at a position along the manufacturing line **310** past the sintering location C may then experience a lower temperature than portions of the tape **314** at the sintering location C and/or than portions of the tape **314** at the binder burn-off location B, such as experiencing room temperature.

[0044] Referring to FIG. **4**, a furnace system **410** includes a guide **412** that defines a passage **414** that extends at least partially through the furnace system **410**, such as fully through a depth LI of the furnace system **410**. In some embodiments, the guide **412** may be a tube or shaft, which may be formed from refractory materials. According to an exemplary embodiment, the passage **414** is generally vertically oriented such that gravity may draw straight or otherwise act along a length of an elongate workpiece (e.g., flexible green tape, ribbon, line; see generally tape **314** of FIG. **3**A) extending through the passage **414**. In some applications of the furnace system **410**, the workpiece may be narrower than the passage **414** and may be positioned within the passage **414** so as to not contact surfaces of the guide **412**. The furnace system **410** may be used in a manufacturing line, such as the manufacturing line **310**.

[0045] According to an exemplary embodiment, the passage **414** of the furnace system **410** has depth dimension L**1** that extends through the furnace system **410**, a width dimension (extending into and out of the FIG. **4**) orthogonal to the depth dimension L**1**, and a gap dimension L**2** that is orthogonal to both the depth dimension L**1** and the width dimension. According to an exemplary embodiment, the depth dimension L**1** of the passage **414** is greater than the width dimension, and the width dimension is greater than the gap dimension L**2**. According to an exemplary embodiment, the gap dimension L**2** is at least 1 millimeter, such as at least 2 millimeters, at least 5 millimeters, and/or no more than 500 centimeters. In some embodiments, the width and gap dimensions are equal to one another such that the passage **414** is cylindrical.

[0046] Referring to FIG. **4**, the furnace system **410** includes a binder burn-off location B' and a sintering location C'. The burn-off location B' is configured to burn binder material from the workpiece and the sintering location C' is configured to at least partially sinter the workpiece. According to an exemplary embodiment, the furnace system **410** includes a heat source **416**, such as an electric resistance heating element, gas or oil burners, or other sources of heat. In some embodiments, the heat source **416** surrounds at least a portion of the sintering location C' and/or is separated from the burn-off location B', such as by barriers or walls **418**, which may be formed from refractory material. According to an exemplary embodiment, the heat source **416** of the furnace system **410** is positioned above or below the burn-off location B'. Accordingly, heat may synergistically pass from the sintering location C' to the binder burn-off location B'. In other embodiments, the burn-off location B may have a heat source that is separated from the sintering location C'.

[0047] The workpiece, prior to entering the binder burn-off location B' may experience a first temperature, such as room temperature (e.g., 25° C.). Near the binder burn-off location B', the temperature experienced by the workpiece may be greater than room temperature, such as at least 200° C., at least 400° C.'. As the workpiece nears and passes the sintering location C', the temperature experienced by the workpiece may be greater still than that experienced by workpiece near the binder burn-off location B', such as at least 800° C., at least 1000° C. Portions of the workpiece beyond the sintering location C', on the side of the sintering location C' opposite to the binder burn-off location B', may then experience a lower temperature, such as experiencing room temperature.

[0048] Referring now to FIG. **5**, a cast of 3 mole-percent Yttria-Stabilized Zirconia (3YSZ) green ceramic may be produced, as described in U.S. Pat. No. 8,894,920. In one example, from the cast, a green tape **512** of material, 2.5 cm wide by 5 m long was cut. The green tape **512** was wound onto a cylindrical roller **514** and was then fed at a controlled rate of 2 inches per minute into a furnace system **516**, as shown in FIG. **5** (see also furnace system **410**, as shown in FIG. **4**). The sintering location C" of the furnace system **516** was held at 1200° C. A binder burn-off location B" was insulated and built out of alumina fiberboard to provide a region for binder burnout. The binder burn-off location B" was heated by hot gasses exiting the sintering location C' of the furnace system **516**.

[0049] In the configuration **510** shown, Applicants have found that a 10 inch long binder burn-off location B" (shown with length in the vertical direction) allows the tape **512** to be successfully fed at up to about 3 inches per minute. The sintering location C" of the furnace system **516** shown is twelve inches, resulting in a total time in the sintering location C" of about four to six minutes. At the exit of the furnace system **516**, the 3YSZ tape **512'** is partially sintered, having a relative density of about 0.65. The 3YSZ tape **512'** has sufficient strength for handling, is flexible, and is about 40 micrometers thick. As shown in FIG. **5**, several meters of sintered tape **512'** have been reoriented on a supportive plastic carrier film **518**.

[0050] Applicants have found that the binder burn-off location B" should be at a temperature in the range of about 200 to 600° C. range for polyvinyl butyral (PVB) binder. Applicants have found that sufficient length of this binder burn-off location B" may also allow high tape speed through the furnace system **516** because if the binder burn-off location B" too short, binder may be removed at an excessive rate, which may cause uncontrolled binder elimination and failure of the tape **512**. Further, Applicants have found the length of the binder burn-off location B" relates to the rate at which the tape **512** may be successfully sintered. According to an exemplary embodiment, the length of the binder burn-of location B" is at least 2 inches and/or no more than 50 inches, such as at least 4 inches and/or no more than 20 inches. In other contemplated embodiments, the binder burn-off location B" may have a length outside of the above ranges.

[0051] Referring still to FIG. **5**, in another example, tape **512**, this time alumina green ceramic, was produced and fired using configuration **510**. The process of casting the tape **512** included steps of batching, milling, de-gassing (or de-airing), filtration, and tape manufacturing. For batching, alumina powder was mixed with a water-based tape casting ingredients including a binder, a dispersant, a plasticizer, and a de-foaming agent. Ingredients used were produced by Polymer Innovations, including an acrylic-based binder that is water soluble.

[0052] For milling, the batched material was milled and mixed in a mill by, for example: ball milling, high shear mixing, attrition milling, vibratory milling, roller milling, and like methods. The milling step de-agglomerates particles and creates a uniform, well-dispersed slurry. In some embodiments, Applicants found an attrition mill (also called a stirred ball mill), from Union Process, may facilitate de-agglomeration by breaking up agglomerates or nano-agglomerates of alumina powder. Applicants believe the attrition mill has benefits over other milling processes and equipment due to high energy input to the materials during the milling process, which allows the batch to be milled to smaller particle sizes in a shorter period of time compared to other techniques, for example, 1 to 3 hours versus 50 to 100 hours with ball milling.

[0053] One Union Process attrition mill used had a total volume of 750 milliliters (mL) and a working volume/capacity of 250 mL. The tank was loaded with 130 mL of slurry and 740 grams of 2 mm 99.9% pure alumina media (i.e., grinding media). The tank was water cooled to 15° C. during the milling process to avoid overheating and to reduce evaporation of solvent(s). The slurry was initially milled for 5 minutes at 500 revolutions per minute (rpm) to break down large agglomerates, then the speed was increased to 1300 rpm and milled for 1 hour. At the end of milling, the tank was slowed to 170 rpm and a de-foaming agent was added to remove entrapped air. The slurry was then poured through a 80 to 120 mesh screen to remove the milling media from the slurry before de-gassing.

[0054] For de-gassing, such as after milling, Applicants found that the milled media may be strained from the slurry, and the slurry may be de-aired/de-gassed using a vacuum to remove entrapped air from the milled product that may otherwise include bubbles within the mix. De-gassing may be accomplished with a desiccator chamber and then a Mazerustar vacuum planetary mixer. The slurry may be loaded into a desiccator chamber and de-gassed for up to 10 minutes. After the initial de-gassing, the slurry may be loaded into the planetary mixer and operated under vacuum for 5 minutes. Applicants found that an alternative de-gassing procedure, eliminating the Mazerustar mixer, is to use a higher vacuum in the desiccator chamber.

[0055] For filtration, the slurry was filtered to remove any large scale contamination from the mixture. Such contaminates may otherwise give adverse optical properties in the sintered material, for example. Filtering may be accomplished with 50 micrometers, 25 micrometers, 10 micrometers, or 1 micrometer filters. Such filters may be made of, for example, nylon, fiber, or other suitable materials.

[0056] For the tape manufacturing step, samples were cast on a silicone-coated Mylar® film, which was approximately 50 to 150 micrometers thick. Applicants find that the silicone coating provides easy release of the tape material after drying. Other suitable films for tape **512** may be, for example, Teflon®, glass, a metal belt, and like alternative materials. To facilitate the tape manufacturing, the slurry was passed under a doctor blade which had a gap of about 4 to 20 mils (about 100 to 500 micrometers) to form a thin sheet of ceramic tape. Typically an 8 mil (about 200 micrometers) blade height was used. The casting blade was moved across the Mylar® at a speed of 10 mm/sec. The speed may be varied as needed to increase process speed, and to modify the thickness of the tape **512**. After drying, the thickness of the tape was 100 to 150 micrometers. The tape **512** in this state is referred to as "green tape."

[0057] Still referring to FIG. **5**, a 1.2 meter long by 120 micrometer thick and 1.2 centimeter wide tape **512** of was cut out of the green casting described above and released. The tape **512** was wound onto the cylindrical roller **514**. The tape **512** was then fed at a controlled rate of 1 inch per minute into the furnace system **516**, as shown in FIG. **5**. The tape **512** had sufficient strength to hold together under its own weight during binder burn-off. The sintering location C" of the furnace system **516** was maintained at a temperature of 1100 C. At the exit of the furnace system **516**, the alumina tape **512'** was partially sintered, having relative density of approximately 0.7. The fired thickness of the tape **512'** was about 100 micrometers.

[0058] Referring to FIGS. **6A**-**6B**, materials manufactured according to inventive processes disclosed herein and with inventive equipment disclosed herein may be distinguished from materials manufactured according to conventional processes. According to an exemplary embodiment, a sintered article **610** (e.g., sheet, foil) includes a first surface **612** (e.g., top, side) and a second surface **614** (e.g., bottom), which may be opposite to the first surface **612**. The sintered article further includes a body **616** of material extending between the first and second surfaces **612**, **614**.

[0059] A thickness T of the article **610** may be defined as a distance between the first and second surfaces **612**, **614**. A width of the article **610** (see generally width W of sintered sheet **810** of FIG. **8**) may be defined as a first dimension of one of the first or second surfaces **612**, **614** that is orthogonal to the thickness T. A length of the article **610** (see generally width L of sintered sheet **810** of FIG. **8**) may be defined as a second dimension of one of the first or second surfaces **612**, **614** that is orthogonal to both the thickness T and the width. According to an exemplary embodiment, the sintered article **610** is an elongate thin tape of sintered material. Due at least in part to geometry, some such embodiments are flexible, allowing the article **610** to bend around a mandrel or spool (e.g., diameter of 1 meter or less, 0.7 meters or less), which may be beneficial for manufacturing, storage, etc. In other embodiments, the sintered article **610** may be otherwise shaped, such as round, annular, sleeve-or tube-shaped, not have a constant thickness, etc.

[0060] According to an exemplary embodiment, the length of the article **610** is greater than twice the width of the article **610**, such as at least 5 times, at least 10 times, at least 100 times greater. In some embodiments, the width of the article **610** is greater than twice the thickness T of the body, such as at least 5 times, at least 10 times, at least 100 times greater. In some embodiments, the width of the article **610** is at least 5 millimeters, such as at least 10 mm, such as at least 50 mm. In some embodiments, the thickness T of the article **610** is no more than 2 centimeters, such as no more than 5 millimeters, such as no more than 2 millimeters, such as no more than 1 millimeter, such as no more than 500 micrometers, such as no more than 200 micrometers. According to an exemplary embodiment, as green tape is passed into a furnace and allowed to sinter, the sintering occurs nearly uniformly; and length, width and thickness of the sheet may diminish up to approximately 30%. As such, dimensions of green tape disclosed herein may be 30% greater than those described for the sintered articles above. Thin tapes may allow the manufacturing line to operate rapidly because heat from the furnace can quickly penetrate and sinter such tapes. Further thin tapes may be flexible, facilitating bends and changes in direction along the manufacturing line (sec generally FIG. **11** for example).

[0061] According to an exemplary embodiment, the sintered article **610** is substantially unpolished such that either or both of the first and second surfaces **612**, **614** have a granular profile, such as when viewed under a microscope, as shown in the digital image of FIG. **6A** and conceptually shown in the side view of FIG. **6**B. The granular profile includes grains **618** protruding generally outward from the body **616** with a height H (e.g., average height) of at least 25 nanometers and/or no more than 100 micrometers relative to recessed portions of the surface at boundaries **620** between the grains **618**, such as the height H of at least 50 nanometers and/or no more than 80 micrometers. In other embodiments, the height H may be otherwise sized.

[0062] The granular profile is an indicator of the process of manufacturing the sintered article **610** in that the article **610** was sintered as a thin tape, as opposed to being cut from a boule, and that the respective surface **612**, **614** has not been substantially polished. Additionally, compared to polished surfaces, the granular profile may provide benefits to the sintered article **610** in some applications, such as scattering light for a backlight unit of a display, increasing surface area for greater adhesion of a coating or for culture growth. In contemplated embodiments, the unpolished surfaces **612**, **614** have a roughness from about 10 to about 1000 nanometers across a distance of 10 millimeters in one dimension along the length of the article, such as from about 15 to about 800 nanometers. In contemplated embodiments, either or both of the surfaces **612**, **614** have a roughness of from about 1 nm to about 10 μm over a distance of 1 cm along a single axis.

[0063] By contrast, the sintered article **710**, of the same material as sintered article **610**, includes polished surfaces **712**, **714**, where grain boundaries are generally removed due to the polishing. In contemplated embodiments, sintered articles **610** manufactured according to the processes disclosed herein may be polished, as shown in FIGS. **7**A-**7**B; depending upon, for example, the particular intended use of the article. For example, use of the article **610** as a substrate may not require an extremely smooth surface, and the unpolished surface of FIGS. **6**A-**6**B may be sufficient; whereas use of the article as a mirror or as a lens may require polishing as shown in FIG. **7**A-**7**B. However, as disclosed herein, polishing may be difficult for particularly thin articles or those that are thin with large surface areas.

[0064] Applicants believe that sheets of sintered ceramic or other materials cut from boules may not have readily identifiable grain boundaries present on surfaces thereon, in contrast to the article of FIGS. **6**A-**6**B. Applicants further believe that boule-cut articles may typically be polished to correct rough surfaces from the cutting. But, Applicants believe that surface polishing may be particularly difficult or cumbersome for very thin articles of sintered ceramic or other materials, with the degree of difficulty increasing as such articles are thinner and the surface areas of such articles are larger. However, sintered articles manufactured according to the presently disclosed technology may be less constrained by such limitations because articles manufactured according to the present technology may be continuously manufactured in long lengths of tape. Further, dimensions of furnace systems, as disclosed herein, may be scaled to accommodate and sinter wider articles, such as having a width of at least 2 centimeters, at least 5 centimeters, at least 10 centimeters, at least 50 centimeters.

[0065] According to an exemplary embodiment, the sintered article **610** has a granular profile and has consistent surface quality on surfaces **612**, **614** thereof, which may be very different from articles manufactured using setter boards, as discussed in the Background, where one side is typically marked by contact (e.g., adhesions and/or abrasions) from the setter board while the other side may not be exposed to the setter board. In some embodiments, such as where the sintered article **610** is in the form of a sheet or tape (see generally sheet **810** as shown in FIG. **8**), the surface consistency is such that an average area of surface defects per square centimeter of the first surface is within plus or minus fifty percent of an average area of surface defects per square centimeter of the second surface, where "surface defects" are abrasions and/or adhesions having a dimension along the respective surface of at least 15, 10, and/or 5 micrometers, as shown in FIGS. **1-2** for example, such as within plus or minus thirty percent of an average area of surface defects per square centimeter of the second surface, such as within plus or minus twenty percent of an average area of surface defects per square centimeter of the second surface.

[0066] According to an exemplary embodiment, the sintered article **610** has high surface quality, which again may be very different from articles manufactured using setter boards, as discussed in the Background, where adhesions and/or abrasions from the setter board may lower surface quality. In some embodiments, such as where the sintered article **610** is in the form of a sheet or tape (see generally sheet **810** as shown in FIG. **8**), the surface quality is such that, on average per square centimeter, the first and second surfaces both have fewer than 15, 10, and/or 5 surface defects having a dimension greater than 15, 10, and/or 5 micrometers, such as a fewer than 3 such surface defects on average per square centimeter, such as fewer than one such surface defect on average per square centimeter. Accordingly, sintered articles manufactured according to inventive technologies disclosed herein may have relatively high and consistent surface quality. Applicants believe that the high and consistent surface quality of the sintered article **610** facilitates increased strength of the article **610** by reducing sites for stress concentrations and/or crack initiations.

[0067] According to an exemplary embodiment, the article **610**, and the corresponding material of the grains of the green tape, includes polycrystalline ceramic. According to an exemplary embodiment, the article **610** includes (e.g., is, consists essentially of, consists at least 50% by weight of) zirconia, alumina, spinel (e.g., $MgAl_2O_4$, $ZnAl_2O_4$, $FeAl_2O_4$, $MnAl_2O_4$, $CuFe_2O_4$, $MgFe_2O_4$, $FeCr_2O_4$,), garnet, cordierite, mullite, perovskite, pyrochlore, silicon carbide, silicon nitride, boron carbide, titanium diboride, silicon alumina nitride, and/or aluminum oxynitride. In some embodiments, the article **610** is a metal. In other embodiments, the article **610** is glass sintered from powder grains. In some embodiments, the article **610** is an IX glass and/or glass-ceramic. Materials disclosed herein may be synthetic.

[0068] Referring now to FIG. **8**, in some embodiments, a sintered article is in the form of a sheet **810** (e.g., sintered tape) of a material disclosed herein. The sheet **810** includes a surface **814** (e.g., top or bottom) with another surface opposite thereto and a body extending between the two surfaces **814** (see generally sides **612**, **614** and body **616** of article **610** of FIGS. **6**A-**6**B). According to an exemplary embodiment, a width W of the sheet **810** is defined as a first dimension of one of the surfaces **814** orthogonal to the thickness T'. According to an exemplary embodiment, the sheet **810** has at least two generally perpendicular lengthwise side edges **812**. A length L of the sheet **810** is defined as a second dimension of one of the top or bottom surfaces **814** orthogonal to both the thickness T' and the width W. The length L may be greater than or equal to the width W. The width W may be greater than or equal to the thickness T'.

[0069] According to an exemplary embodiment, the thickness T' is no more than 500 micrometers, such as no more than 250 micrometers, such as no more than 100 micrometers, and/or at least 20 nanometers. According to an exemplary embodiment, the sheet **810** has a surface area of at least **10** square centimeters, such as at least **30** square centimeters, such as at least **100** square centimeters, and even exceeding **1000**, **5000**, or even **10,000** square centimeters in some embodiments; or is otherwise sized according to geometries disclosed herein, such as with regard to embodiments of the article **610**. In some embodiments, the sheet **810** has a width W that is less than **1/4**, **1/5**, **1/6**, **1/7**, **1/8**, **1/9**, **1/10** and/or **1/20** the length L thereof. Such geometries may be particularly useful for certain applications, such as for use of the sheet **810** as a substrate of a rectilinear battery and/or for use of the sheet **810** as a surface for growing carbon nanotubes in an oven, where the sheet **810** fills surfaces of the oven, yet does not fill substantial volume of the oven.

[0070] According to an exemplary embodiment, the sheet **810** includes (e.g., is formed from, consists of, consists essentially of, consists more than **50**% of in volume) a material selected from the group consisting of polycrystalline ceramic and synthetic mineral. In other embodiments, the sheet **810** includes glass, metal or other materials, as disclosed herein. Further, according to an exemplary embodiment, the material of the sheet **810** is in a sintered form such that grains of the material are fused to one another (see generally FIG. **6**A). The sheet **810** may have a granular profile (see generally FIGS. **6**A-**6**B) or may be polished (sec generally FIGS. **7**A-**7**B).

[0071] For example, in some embodiments, the sheet **810** is made from alumina powder having a median particle size diameter of from 50 to 1000 nanometers and a BET surface area of from 2 to 30 m^2/g. The sheet **810** is made from a tape-casted alumina powder of from 99.5 to 99.995 weight percent alumina and from about 100 to about 1000 parts per million of a sintering additive, such as magnesium oxide. In some embodiments, the sheet **810** is translucent. The sheet **810** may have a total transmittance of at least 30% at wavelengths from about 300 nm to about 800 nm when the sheet **810** has a thickness of 500 μm or less. In some embodiments, the total transmission through the sheet **810** is from about 50% to about 85% at wavelengths from about 300 nm to about 800 nm when the sheet **810** has a thickness of 500 μm or less. In some embodiments, diffuse transmission through the sheet **810** is from about 10% to about 60% at wavelengths from about 300 nm to about 800 nm when the sheet has a thickness of 500 μm or less. In contemplated embodiments, the sheet **810** may have the above-disclosed transmittance percentages with a wavelength in the above-disclosed ranges but with other thicknesses, such as other thicknesses disclosed herein. Materials disclosed herein other than alumina may also result in such a translucent sintered article.

[0072] Referring to FIG. **9**, a manufacturing line **910** includes a source **912** of green tape **922**, a furnace system **914**, tension regulators **916**, **918**, and a receiver **920** of sintered tape **924**. According to an exemplary embodiment, the source **912** of green tape **922** may be in the form of a roll of the green tape **922**, as may be separately manufactured. From the source **912**, the green tape **922** is directed into a first portion **926** of the furnace system **914** such as by way of a guiding passage **928**. As shown in FIG. **9**, in some embodiments, the green tape **922** is directed along a vertical axis through the furnace system **914** such that the green tape **922** does not contact a setter board and/or surfaces of the furnace system **914**.

[0073] The first portion **926** of the furnace system **914** may include a binder burn-off location (see generally location B of the manufacturing line of FIG. **3**) and a location for partial sintering of the tape **912** (see generally location C of the manufacturing line of FIG. **3**). Accordingly, tape **932** exiting the first portion **926** of the first system **914** may be partially sintered. Tension in the tape **922** through the first portion **926** of the furnace system **914** may be influenced by the tension regulator **916**, which may differentiate tension in the tape **922**, **932**, **924** on either side of the tension regulator **916** along the manufacturing line **910**. As shown in FIG. **9**, below the tension regulator **916** the furnace system **914** includes a second portion **930**.

[0074] According to an exemplary embodiment, tension in the tape **932**, **924** between the tension regulators **916**, **918** may be greater than tension in the tape **922**, **932**, **924** not between the tension regulators **916**, **918**. In some embodiments, increased tension between the tension regulators **916**, **918** may be used to hold the tape **932** flat as the tape **932** is sintered in the second portion **930** of the furnace system **914**. For example, partially sintered tape **932** may be flexible enough to bend and/or flatten by tension in the tape **932** between the tension regulators **932**, **918**, yet the partially sintered tape **932**, due to the bonds of partial sintering, may be strong enough to support the tension without failure. Put another way, in the second portion **930** of the furnace system **914**, the partially sintered tape **932** is sintered to a final density and held under enough tension to flatten the sheet, tape or ribbon, eliminating curl, warp, camber, etc. that may appear with unconstrained sintering. For example, Applicants found a **1** centimeter wide partially-sintered ribbon of zirconia or alumina was able to support greater than **1** kilogram of tension, about **20** megapascals, without failure.

[0075] Accordingly, referring once more to FIG. **8**, in contemplated embodiments, the unmodified surface of the sheet **810** has a flatness of from about 0.1 μm to about 50 μm over a distance of 1 cm along a single axis, such as along the length of the sheet **810**. Such flatness, in combination with the surface quality, surface consistency, large area, thin thickness, and/or material properties of materials disclosed herein, may allow sheets, substrates, sintered tapes, articles, etc. to be particularly useful for various applications, such as tough cover sheets for displays, high-temperature substrates, flexible separators, and other applications.

[0076] Due to limited ability of garnet to creep or relax under pressure load, garnet may be difficult to reshape after the garnet has been manufactured. Accordingly, garnet may be difficult to manufacture thin and flat according to conventional processes. To do so, those of skill in the art have typically sandwiched green bodies between flat refractory surfaces, which typically results in many surface defects on both sides of the sintered article. Accordingly, the presently disclosed technology is believed to be particularly useful when manufacturing thin sheets of synthetic garnet as disclosed herein.

[0077] Referring to FIG. **10**, a manufacturing line **1010**, similar to manufacturing line **910** of FIG. **9**, includes a source **1012** of green tape **1022**, a furnace system **1014** having two separate portions **1026**, **1030**, tension regulators

1016, **1018**, and a receiver **1020** of sintered tape **1024**. However, with the manufacturing line **1010**, the green tape is continuously manufactured on the line **1010**. Further, the sintered tape **1024** is cut into strips **1032** (e.g., at least 5 centimeters long, at least 10 centimeters long, and/or no more than 5 meters long, no more than 3 meters long) as the sintered tape **1024** emerges from the second portion **1030** of the furnace system **1014**. The strips **1032** subsequently may be stacked, packaged, and shipped.

[0078] Referring to FIG. **11**, a manufacturing line **1110** includes a source of tape **1112** (e.g., green tape). The source is in the form of a spool **1114** of the tape **1112**, where the tape **1112** is initially on a polymeric backing **1116**, such as Mylar. As the tape **1112** comes, generally horizontally, off the spool **1114** (e.g., within 30-degrees of horizontal, within 10-degrees of horizontal), the polymeric backing **1116** is pulled off the tape **1112** at a separation location **1118** and wound onto a separate spool **1120**. The tape **1112** then passes over an air bearing **1122** and is gradually redirected, with a controlled amount of sag, into a first guide **1124**, which orients the tape **1112** generally vertically (e.g., within 30-degrees of vertical, within 10-degrees of vertical).

[0079] Following the first guide **1124**, the tape **1112**, in a green form, moves upward into a first furnace **1126** (see generally furnace **410** as shown in FIG. **4**). In some embodiments, the first furnace **1126** is a lower temperature furnace that chars or burns organic binder off of the tape **1112** to form an unbound section of the tape **1112**. The first furnace **1126** may also partially sinter the resulting unbound section of the tape **1112**, to form a partially sintered section **1128** of the tape **1112**. After passing through the first furnace, the tape **1112** may be directed through a second guide **1130**. The first and second guides **1124 1130** align the tape **1112** with a passage through the first furnace **1126** so that the tape **1112** does not contact surfaces of the first furnace **1126**, thereby reducing the number of adhesion and abrasion related surface defects. Such a tape **1112** may still have some defects, such as due to contact with errant particles, etc.

[0080] According to an exemplary embodiment, following the second guide **1130**, the partially sintered section **1128** of the tape is routed over a wheel **1132**. In some embodiments, the wheel **1132** has a low-friction surface **1134**, over which the partially sintered section **1128** slides. A temperature differential between the wheel **1132** and the partially sintered section **1128** may help inhibit sticking or adhesion between the wheel **1132** and the partially sintered section **1128**. According to an exemplary embodiment, the wheel **1132** rotates to control tension in the tape **1112**, such as by providing different tension in the tape **1112** on either side of the wheel **1132**.

[0081] For example, in some instances, the wheel **1132** rotates (e.g., clockwise) against the direction (e.g., counterclockwise) that the tape **1112** slides over the wheel **1132**, decreasing tension in the tape **1112** on the side of the wheel **1132** from which the tape **1112** is coming and increasing tension in the tape **1112** on the side of the wheel **1132** to which the tape **1112** is going, with the increased tension being maintained on a distal end of the tape **1112** by a tension regulator, such as a spool receiving the tape **1112** (see generally FIGS. **3** and **9**), a robotic arm drawing the tape **1112** (see generally FIG. **10**), rollers, etc. Tension in the tape **1112** as the tape **1112** passes through a second, possibly higher temperature, furnace **1136**, holds the tape **1112** flat as the tape **1112** is fully sintered.

[0082] The construction and arrangements of the manufacturing line, equipment, and resulting sintered articles, as shown in the various exemplary embodiments, are illustrative only. Although only a few embodiments have been described in detail in this disclosure, many modifications are possible (e.g., variations in sizes, dimensions, structures, shapes, and proportions of the various elements, values of parameters, mounting arrangements, use of materials, colors, orientations) without materially departing from the novel teachings and advantages of the subject matter described herein. Some elements shown as integrally formed may be constructed of multiple parts or elements, the position of elements may be reversed or otherwise varied, and the nature or number of discrete elements or positions may be altered or varied. The order or sequence of any process, logical algorithm, or method steps may be varied or re-sequenced according to alternative embodiments. Other substitutions, modifications, changes and omissions may also be made in the design, operating conditions and arrangement of the various exemplary embodiments without departing from the scope of the present inventive technology.

[0083] Referring momentarily again to FIG. **6**, the granular profile includes grains **618** protruding generally outward from the body **616** with a height H (e.g., average height) of at least 5 nanometers, such as at least 10 nanometers, such as at least 20 nanometers, such as at least 25 nanometers and/or no more than 200 micrometers, such as no more than 100 micrometers, no more than 80 micrometers no more than 50 micrometers relative to recessed portions of the surface at boundaries **620** between the grains **618**.

[0084] Referring to FIG. **12**, a manufacturing line **1210** for partial sintering includes a source of tape **1212** (e.g., green tape). The source is in the form of a spool **1214** of the tape **1212**, where the tape **1212** is initially on a polymeric backing **1216**, such as Mylar. In some such embodiments, the tape **1212** comes off the spool **1214** and over a roller **1244** and a vacuum hug drum **1242**, then the polymeric backing **1216** is pulled off the tape **1212** at a separation location **1218** and is tensioned by a tension device **1240**, passing over a roller **1246** and wound onto a separate spool **1220**. The tape **1212** (without backing **1216**) then passes into the binder burnout section B''' of the furnace **1226**. In some such embodiments, the tape **1212** enters oriented generally vertically and/or without contacting the furnace **1226**.

[0085] Following the separation location **1218**, the tape **1212**, in a green form, moves downward into the furnace **1226** (see also generally furnace **410**, as shown in FIG. **4**). In some embodiments, the binder burn out section B'''' of furnace **1226** is a lower temperature furnace that chars or burns organic binder off of the tape **1212** to form an unbound section of the tape **1212**. A higher temperature portion C''' of the furnace **1226** may also partially sinter the resulting unbound section of the tape **1212**, to form a partially sintered section **1228** of the tape **1212**, shown in FIG. **12** passing out of the furnace **1226**.

[0086] After passing through the furnace **1226**, the tape **1212** may be directed drawn across a roller **1252** that acts as second guide. The separation location **1218** and exit roller **1252** may align the tape **1212** with a passage through the furnace **1226** so that the tape **1212** does not contact surfaces of the furnace **1226**, thereby reducing the number of adhesion and abrasion related surface defects. According to an exemplary embodiment, the separation location **1218** and roller **1252** or other guide at or near an exit of the furnace **1226** are generally vertically aligned with one another, such as along a line that is within 15-degrees of vertical, such as within 10-degrees.

[0087] Applicants note that such a tape **1212** may still have some defects, such as due to contact with errant particles, particles in the air, etc. The exit roller **1252** may be made of a low friction polymeric material. After passing over the exit roller **1252**, the partially sintered tape can be wound on a receiving spool **1250**.

Example 1

[0088] A 90 foot long tape of partially sintered zirconia tape was made with an apparatus generally as shown in FIG. **12**. The green tape was made in manner similar to that described in U.S. Pat. No. 8,894,920 B2 using Tosho (Japan) zirconia powder 3YE. The green tape was cast at a width larger than about 20 cm and thickness of the green tape was about 25 micrometers. The tape was then manually slit to about 15 mm in width using circular razor blades. The green tape was passed from a pay-out spool (see generally spool **1214** in FIG. **12**) over the separation location (see separation location **1218** in FIG. **12**) and through a binder burn-out chimney (see burn-out section B'''' of furnace **1226** in FIG. **12**), through a transition zone (see zone X''' in FIG. **12**) and into a higher temperature furnace (e.g., section C'' of the furnace **1226** in FIG. **12**).

[0089] Referring to the Example 1 in the context of FIG. **12**, at the separation location, **1218**, the ceramic tape **1212** was released from the carrier film **1216**. The carrier film **1216** was run over a tensioning device **1240** and on to a take-up spool **1220**. The binder-burn out zone B''' was passively heated by hot air from the furnace section C'''. The channel in the furnace and binder burnout chimney used for Example 1 was made from ceramic fiber board in parallel plates with a gap of between 0.125 and 0.5 inches between the plates (see generally gap **414** and L**2** of FIG. **4**). The width of the channel orthogonal to the gap was about 3.5 inches. The length of the binder burnout zone was about 17 inches and the length of the furnace below the binder burnout zone was 24 inches.

[0090] Applicants note that the green tape can be threaded into the furnace either cold or hot. If threading hot, Applicants set a temperature near 1000° C. for the furnace and a tape speed of 1 inch/min, when sintering or partially sintering 3YSZ, 3 mol % yttria-stabilize zirconia, tetragonal-phase zirconia polycrystal "TZP", and/or alumina or other ceramics with similar sintering temperatures. After threading hot, after the tape comes out of the bottom of the furnace, the temperature can be increased and the speed of the tape increased. If threading cold, Applicants recommend moving (i.e., transporting, conveying) the tape at a low speed, 0.25 to 1 inch/min., during heat up through the furnace.

[0091] In this Example 1, the tape was threaded hot, and after threading, the furnace was heated to and set at 1200 C, and the tape was then moved at a speed of 8 inches/min. through the furnace. The binder burnout chimney was at a temperature of between about 100 to 400° C. The green tape was transported through the furnace for was over 2.25 hours, and about 90 feet of continuous length of partially sintered tape was obtained.

[0092] Sintering shrinkage in the width was about 9.5-10.5%. The partially sintered tape was rolled on a 3.25 inch diameter spool without cracking.

Example 2

[0093] A 65 foot length of partially sintered zirconia tape was made with an apparatus similar to that shown in FIG. **12**, where the green tape was again made in manner similar to that described in U.S. Pat. No. 8,894,920 using Tosho (Japan) Zirconia powder 3YE. The green tape was cast at a width larger than about 20 cm. The thickness of the green tape was about 25 micrometers. The green tape was then manually slit to about 52 mm in width using circular razor blades.

[0094] Next, the green tape was passed from the pay-out spool over the separation location and through a binder burn-out chimney, through a transition zone, and into a higher temperature, actively-heated furnace (e.g., furnace **1226**). The binder-burn out zone was passively heated by heated air from the furnace. The channel in the furnace and binder burnout chimney was (again) made from ceramic fiber board in parallel plates with a gap of between ⅛ and ½ inch between the plates. The width of the channel was about 3½ inches. The length of the binder burnout zone was about 17 inches and the length of the furnace was 24 inches.

[0095] In this Example 2, after threading, the furnace was heated to 1000° C., 1025° C., 1050° C., 1075° C., and 1100° C. while the tape was moved at a speed of 2 inches/min. therethrough. The binder burnout chimney was at a temperature of between about 100 and 400° C. Tape was run at the individual furnace temperatures for about an hour for each temperature. The furnace was run for over 6.5 hours, and over continuous 65 feet (green) of partially sintered tape was run through the furnace.

[0096] Sintering shrinkage across the width of the tape was dependent on furnace temperature and, as listed in the following Table 1. Some out of plane deformation was encountered and variation of the sintering shrinkage in the Table is partially due to the out of plane deformation of the tape.

TABLE 1

52 mm Green Tape	
Temperature	Shrinkage %
1000° C.	2.08%
1000° C.	1.56%
1025° C.	2.34%
1050° C.	3.47%
1075° C.	4.28%
1100° C.	5.61%

[0097] In various embodiments disclosed herein, such as for materials and systems disclosed herein, the temperature of the higher-temperature furnace is at least 800° C., such as at least 1000° C. Green tap is passed therethrough at a rate of at least 1 inch/min, such as at least 2 inch/min. Rate may be increased by increasing the length of the furnace, for example. Shrinkage of green tape passing therethrough was at least 1.5%, such, as at least 2% in some embodiments and/or no more than 20%, such as no more than 15%.

Example 3

[0098] About a 60 foot length of partially sintered zirconia tape was made with an apparatus, similar to that shown in FIG. **12**, where the green tape was again made in manner similar to that described in U.S. Pat. No. 8,894,920 using

Tosho (Japan) zirconia powder 3YE. The green tape was cast at a width larger than about 20 cm. The thickness of the green tape was about 25 micrometers. The tape was then manually slit to about 35 mm in width using circular razor blades.

[0099] The green tape was passed from the pay-out spool over the separation location and through a binder burn-out chimney, through a transition zone and into the furnace. The binder-burn out zone was passively heated by heated air from the furnace. The channel in the furnace and binder burnout chimney was made from ceramic fiber board in parallel plates with a gap of between ⅛ and ½ inch between the plates. The width of the channel was about 3½ inches. The length of the binder burnout zone was about 17 inches and the length of the furnace was 24 inches.

[0100] In this Example 3, after threading, the furnace was heated to 1100° C., 1150° C. and 1200° C. while the tape was moved at a speed of 4 and 6 inches/minute. The binder burnout chimney was at a temperature of between about 100° C. and 400° C. About ten feet of the tape at each temperature and respective tape speed condition was spooled on to a 3.25 diameter spool after partial sintering, without breaking.

[0101] Sintering shrinkage was measured and is listed in the following Table 2, where some out of plane deformation was encountered and variation of the sintering shrinkage in the Table is partially due to the out of plane deformation of the tape.

TABLE 2

Temp (° C.)	Speed (in/min) 35 mm green width	Shrinkage Percent
1100	4	5.05
1100	6	5.16
1150	4	8.09
1150	6	6.73
1200	4	12.01
1200	6	11.20

Example 4

[0102] A 175 foot length of partially sintered zirconia tape was made with an apparatus shown in FIG. **12**. Zirconia green tape was made as described above, but tape was manually slit to about **15** mm width using circular razor blades. The tape was passed from the pay-out spool over the separation location and through a binder burn-out chimney, through a transition zone and into the furnace. Temperatures of 1100° C. to 1200° C. and speeds of 4, 6, or 8 inches/min. were run. The binder burnout chimney was at a temperature of between about 100 and 400° C., and a total of 175 feet (green) of partially sintered tape was made.

[0103] Sintering shrinkage was measured and is listed in the following Table 3, where some out of plane deformation was encountered and the variation of the sintering shrinkage in the table is partially due to the out of plane deformation of the tape. Tape made at 1200 C and 8 inches per minute, had an average out of plane flatness over the length and width of the tape, of about 0.6 mm overall, when measured over 1200 mm along the length of the tape.

TABLE 3

Temp (° C.)	Speed (IPM) 15 mm green width	Shrinkage Percent
1100	4	5.38
1100	6	6.70
1100	8	5.07
1150	4	8.58
1150	6	8.16
1150	8	7.25
1200	4	11.89
1200	6	11.33
1200	8	10.07

Example 5

[0104] A 147 foot length of partially sintered zirconia tape was made with an apparatus similar to that shown in FIG. **12**. Zirconia green tape was made as described above and slit to about 15 mm using circular razor blades. The tape was processed as described above, except where, after threading, the furnace was heated to and set at 1200° C., and the tape was moved at a speed of 8 inches/minute. The binder burnout chimney was at a temperature of between about 100° C. and 400° C. The green tape was moved through the furnace for over 3 hours, and over 147 feet of continuous length (green) of partially sintered tape was obtained.

[0105] Referring now to FIG. **13**, a manufacturing line **1310** for partial sintering includes a source of partially sintered tape **1312**. The source is in the form of a spool **1314** of the partially sintered tape **1312**, where the tape **1312** may have an interleaf material. As the tape **1312** comes off the spool **1314** and over a roller **1342**. Plates **1346** of high temperature material form a narrow channel in the furnace **1326**.

[0106] The tape **1212** then passes into the furnace **1326**, the tape **1312** being generally vertical and/or without contacting the furnace and/or without contacting the furnace along a central portion thereof. In contemplated embodiments, edges of the tape may contact guides or surfaces in the furnace, but may later be removed to provide a low-defect center portion of the tape, as disclosed herein. In some such embodiments, the lengthwise edges of the tape include indicia of cutting, such as laser or mechanical marks.

[0107] After passing through the furnace **1326**, the final sintered tape **1329** may be drawn across a tension device **1340**. The input roller **1342** and tension device, **1340**, are generally linearly-aligned with the channel through the furnace **1326** so that the tape **1312** does not contact surfaces of the furnace **1326**, in some such embodiments, thereby reducing the number of adhesion-and abrasion-related surface defects as described herein. After passing over the tension device **1340** the final sintered tape passes over two rollers **1344**, and through a conveyance device **1360** (e.g., rollers, bearing, treads). After the conveyance device **1360** the final sintered tape can be spooled with or without interleaf material.

[0108] Referring to FIG. **14**, a manufacturing line **1410** for partial sintering includes a source of partially sintered tape **1412**. The source is in the form of a spool **1414** of the partially sintered tape **1412**, where the tape **1412** may have an interleaf material. As the tape **1412** comes off the spool **1414** the tape **1212** then passes into the furnace **1426**, the tape **1412** being generally vertically oriented. A tensioner (e.g., weight **1460**, rollers), is attached to the partially sintered tape to draw the tape and/or hold the tape flat during the sintering. In contemplated embodiments, the weight **1460** may be a length of the tape itself.

[0109] Surprisingly, as disclosed above, Applicants have found that a short length of the green tape, with the binder burned out, can support some tension, without the tape falling apart. The tensile strength of the section with burned-out binder, but prior to entering the higher-temperature furnace, is just a fraction of the tensile strength of ideal, fully-sintered tape of the same material and formed from a green tape of the same dimensions and composition, such as less than 20%, such as less than 10%, such as less than 5%, but is still positive, such as at least 0.05%.

Example 6

[0110] Partially sintered tape of 15 mm (green) width was made as described in Example 1. A roll of this partially sintered tape, 15 mm wide (green), about 25 micrometers thick (green), was then put on the apparatus similar to system **1310** shown in FIG. **13** (e.g., second furnace, second sintering location). The ceramic plates, **1346**, were made of silicon carbide. The gap between the plates was 2 to 8 mm and the width of the plates was 4 inches. The outside dimension of the furnace was 21 inches long. The furnace was heated to 1400 C. (e.g., at least 100° C. greater temperature than the furnace of Example 1, such as at least 200° C. greater, 400° C. greater).

[0111] In Example 6, the partially sintered tape (from Example 1) was rapidly threaded by hand into the 1400° C. furnace at greater than 1 foot/minute. Enough tape was provided from the spool **1314** that the tape **1312** was wound around the tensioning device **1340**, through two rollers **1344**, and through a conveyance device **1360**.

[0112] After threading, the tape was run at 2 inches per minute. Less than 50 grams of tension was put on the sintering tape by the tension device **1340**. About 9 inches of dense, final sintered tape was produced (see, e.g., fully sintered tape **2010** of FIGS. **17-22**). The tape was translucent, text could be read through it if the text was placed in contact with the tape (see fully sintered tape **2010** of FIGS. **17-18** and compare to partially sintered tape **2012** of FIGS. **17-18**). The tape did have some white haze from light scattering, probably from a slight porosity (e.g., porosity less than 1%, such as less than 0.5%, and/or at least 0.1%).

[0113] Cross tape shrinkage was about 24%. Batch fired material of the same type of tape casting had a sintering shrinkage of about 23%, +/− about 0.5%. Although the partially sintered tape used for this experiment had some out of plane deformation, after final sintering, the tape was flat in the direction of tape motion. There was some "C-shaped" curl in the cross web (tape) direction. An area of 1 cm×1 cm of the fully sintered tape was examined by optical microscopy at 100-times magnification. Both sides of the final sintered tape were examined. No adhesion or abrasion defects typical of setter boards were found.

[0114] As seen in FIG. **15**, the final sintered tape can be bent to a radius of less than about, 2.5 cm

Example 7

[0115] A second-stage sintering apparatus, similar to that shown in FIG. **14** was used. The furnace was only about 4 inches high, with a 2-inch hot zone. Partially sintered tape of 30 mm wide (green) was used that was made in manner similar that described for Example 3. Prior to partial sintering, the tape was about 25 micrometers thick. A spool of the partially sintered tape was put over the furnace, where the furnace had a narrow gap of 3/16th of an inch and 3.5 inches wide in the top and bottom furnace insulation, to allow the tape to pass through. The tape was threaded cold through the gaps and a weight of 7.5 grams was attached (see generally FIG. **14**). The furnace was heated to 1450° C., and tape motion was started when the furnace achieved 1450° C. The tape was run from top to bottom at a speed of 0.5 inches per minute. About 18 inches of fully-sintered sintered zirconia tape was made. The zirconia tape was translucent. In Example 7, with the 4 inch furnace, the tape, as well as the fully sintered portion thereof, was longer than the furnace.

[0116] Referring to FIGS. **15-16**, for context and comparison purposes, green tape (3 mol % yttria-stabilize zirconia) was made as described in the above Examples and sintered using conventional sintering processes, including use of an alumina setter board to support the green tape during the sintering, to form a ceramic tape **3010**. Surface defects due to adhesion and abrasion from the setter board can be seen at 100-times magnification, as shown in FIG. **15**. Many of the adhesion or abrasion-caused defects form pin holes in the sintered sheet because the sheet is so thin, on the order of 25 micrometers. As shown in FIG. **15**, the defects due to adhesion and abrasion from the setter board are generally oblong in a common direction to one another,

[0117] As discussed above, setter-induced defects are typically surface features caused by sintering shrinkage of a green tape in contact with a setter board, where the ceramic drags portions of itself across the setter board during sintering shrinkage. The result is that the supported side of the resulting sintered article has surface defects, such as drag grooves, sintered debris, impurity patches, etc. transferred from refractory material of the setter board to the sintering article, and pits in the surface where the setters pull out material from the sintered article. Minimizing such setter defects is important when the ceramic article is has thin films deposited on it. If the layer thickness of the thin film or films is similar to a setter defect dimension, the thin film may have pin holes or have the setter defect traversing the thin film layer(s).

[0118] Compare the ceramic tape **3010** of FIGS. **15-16**, to the ceramic tape **2010** of FIGS. **17-22**, manufactured using the technology of the present disclosure; especially as shown in FIGS. **19-20**, which are at the same magnifications 100× and 500×, respectively, of FIGS. **15-16**, and are from a green tape made in the same way as the tape used for FIGS. **15-16**. More specifically, the ceramic tape **2010** was continuously sintered, as disclosed herein, run at 1400° C. at a rate of 2 inches per minute through a secondary furnace as described in the Examples, with a silicon carbide central channel. Comparing ceramic tape **3010** to ceramic tape **2010**, both tapes show various indicia of casting at the surface, such as elongate, rolling stria and sloping (hills/valleys). The ceramic tape **3010** shows numerous setter-related defects: bonded particles, pull-out and setter-drag defects, such as where setter drag produces characteristic damage patterns in regions due to gouging of the surface as the shrinking tape drags across the setter surface, as discussed herein.

[0119] Referring to FIGS. **15-16** and FIGS. **19-20**, bonded particles, larger than 5 μm in a cross-sectional dimension thereof, were easily observed at 100× in optical examination of the surfaces (see FIGS. **15** and **19**). More specifically, across an area of about 8 cm^2, one such particle was observed on the surface of the ceramic tape **2010** sintered using the technology disclosed herein, while across an equal area of about 8 cm^2, eight such particles were observed on the surface of the ceramic tape **3010**. Applicants believe the ceramic tape **3010** had more bound particles due to contact with the setter, while the ceramic tape **2010** had a smaller number of bound surface particles, which may have been present due to adhesion of particles in the furnace atmosphere. This small number of bound surface particles on the ceramic tape **2010** may be further reduced in future process embodiments that use filters or other processes to remove or reduce particles in the furnace atmosphere.

[0120] According to an exemplary embodiment, tape manufactured according to the present disclosure has, on average over the surface thereof, fewer than 5 bonded particles, larger than 5 μm in a cross-sectional dimension thereof, per 8 cm^2, such as fewer than 3 such particles, such as fewer than 2 such particles.

[0121] According to an exemplary embodiment, a sheet of sintered ceramic, as disclosed herein, has a thickness of less than 50 micrometer and fewer than 10 pin holes, having a cross-sectional area of at least a square micrometer (or fewer than 10 pin holes over the full surface, if the surface area is less than a square micrometer), per square millimeter of surface on average over the full surface, such as fewer than 5 pin holes, fewer than 2 pin holes, and even fewer than fewer than 1 pin hole per square millimeter of surface on average over the full surface.

[0122] Referring to FIGS. **19-20**, the ceramic tape **19** has a granular surface with bulges **2014**. The bulges have longest dimensions on the order of 100 or more micrometers. The bulges are generally oblong, such as having major axes oriented generally in the same direction as one another, such as 90% within 15-degrees of a direction D, such as within 10-degrees. The bulges may be distinguished from setter-induced surface defects, such as abrasion and adhesion, because the bulges are generally smoothly rolling and continuously curving from adjoining surface, as opposed to being defined by or including disjointed or discontinuous borders on a surface as is characteristic of an adhered particle or an abrasion caused by a setter. The bulges may be indicia of at least some processes disclosed herein, such as due to the less-constrained sintering processes. Other embodiments may not include such bulges, such as if the tape is tensioned axially and widthwise during sintering, which may be done via tensioners (e.g., rollers, treads, wheels, mechanical tensioners or other such elements).

[0123] Referring now to FIGS. **21-22**, a ceramic tape **4010** has been manufactured according to the processes disclosed herein, without a setter board. The material of the tape **4010** is 3 mol % yttria-stabilize zirconia, tetragonal-phase zirconia polycrystal "TZP." The width of the tape is between 12.8 to 12.9 mm. The portion shown is from a 22 inch long piece of tape. The thickness of the tape is about 22 micrometers. Incidentally, the white spots are marker markings on the tape that the scanner did not recognize.

[0124] For comparison purposes, the tape was fully sintered below the line, and only partially sintered above the dashed line L. SEC**1**, SEC**2**, SEC**3**, SEC**4** are profiles of the top surface of the ceramic tape **4010**. The profiles show that the tape has some "C-shaped" curvature about the lengthwise axis (shown as X-axis in FIG. **21**). The camber in the tape is decreased by fully sintering, under tension, as disclosed herein. As can be seen, maximum height of the tape decreased by about 100% from about 1.68 mm to between 0.89 and 0.63 mm. Applicants believe that through present processes and/or further process refinements, such as increased tension or changing process speeds, that the maximum height of the fully-sintered tape resting flat on a flat surface would be less than 1.5 mm, such as less than 1 mm, such as less than 0.7 mm, such as ideally less than about 100 micrometers, such as for a tape having a width of about 10 to 15 mm.

[0125] In contemplated embodiments, the tapes described herein may be wound on a spool, as shown in the Figures, to form a roll of tape. The spool may have a diameter of at least about 0.5 cm, such as at least about 2.5 cm, and/or no greater than 1 m, with the length of the tape being at least 1 m, such as at least 10 m, and having a width and thickness as described herein, and/or such as a width of at least 10 mm and/or no greater than 20 cm and a thickness of at least 10 micrometers and/or no greater than 500 micrometers, such as no greater than 250 micrometers, such as no greater than 100 micrometers, such as no greater than 50 micrometers.

1-13. (canceled)

14. The ribbon of claim **21**,

wherein the ribbon has fewer than 1 pin holes having a cross-sectional area of at least a square micrometer per square millimeter of surface on average over full surfaces thereof.

15. The ribbon of claim **14**, wherein the thickness is less than 50 micrometers.

16. The ribbon of claim **14**, further comprising:

a first surface, a second surface, and a body extending therebetween, wherein the body comprises the ceramic grains fused to one another:

wherein the first and second surfaces each have a granular profile, wherein the granular profile includes grains with a height in a range from twenty-five nanometers to one-hundred-and-fifty micrometers relative to recessed portions of the first and second surfaces at boundaries between the respective grains; and

wherein the ribbon has high surface quality such that the first and second surfaces both have at least a square centimeter of area having fewer than ten surface defects from adhesion or abrasion with a dimension greater than five micrometers.

17. (canceled)

18. The ribbon of claim **16**, wherein the ribbon has high surface quality such that the first and second surfaces both have at least a square centimeter of area having fewer than 10 surface defects from adhesion or abrasion with a dimension greater than 5 micrometers.

19. The ribbon of claim **16**, wherein the ribbon has high surface quality such that the first and second surfaces both have at least a square centimeter of area having fewer than 10 surface defects from adhesion or abrasion with a dimension greater than 5 micrometers.

20. (canceled)

21. A sintered polycrystalline ceramic ribbon, comprising:

ceramic grains fused to one another;

a length of at least 10 m,

a thickness of at least 20 nm and no more than 100 μm,

a width at least 10 times the thickness, and wherein the length is at least 100 times greater than the width, and wherein the ribbon has fewer than 10 pin holes having a cross-sectional area of at least a square micrometer per square millimeter of surface on average over full surfaces thereof.

22. The ribbon of claim **21**, wherein the thickness is less than 50 micrometers.

23. (canceled)

24. The ribbon of claim **21**,

wherein the width is at least 5 mm and no greater than 20 cm.

25. The ribbon of claim **24**, wherein the thickness is at least 10 μm and less than 50 μm.

26. The ribbon of claim **25**, wherein the ribbon has fewer than 1 pin hole having a cross-sectional area of at least a square micrometer per square millimeter of surface on average over full surfaces thereof.

27. The ribbon of claim **24**, wherein porosity of the ribbon is less than 1%.

28. The ribbon of claim **24**, wherein the ceramic grains are lithium garnet.

29. The ribbon of claim **28**, wherein the ribbon has a surface area exceeding 1000 cm^2.

30. The ribbon of claim **28**, wherein the ribbon is flexible enough to be wound on a mandrel of 0.7 m diameter.

31. The ribbon of claim **28**, wherein surfaces thereof have a roughness in a range of 10 nanometers to 1000 nanometers across a distance of 10 millimeters along the length of the ribbon.

32. The ribbon of claim **28**, wherein the ribbon has flatness in a range of 0.1 μm to 50 μm over a distance of 1 cm along a single axis.

33. The ribbon of claim **24**, wherein the ribbon can support 20 megapascals of tension without failure.

34. A sintered polycrystalline ceramic ribbon, comprising:

ceramic grains fused to one another;

a length of at least 10 m,

a thickness of at least 10 μm and less than 100 μm,

a width at least 10 times the thickness, and wherein the length is at least 100 times greater than the width,

wherein the ribbon has fewer than 10 pin holes having a cross-sectional area of at least a square micrometer per square millimeter of surface on average over full surfaces thereof; and

wherein porosity of the ribbon is less than **1**%.

35. A sintered polycrystalline ceramic ribbon, comprising:

ceramic grains fused to one another;

a length of at least 10 m,

a thickness of at least 10 μm and less than 100 μm,

a width at least 10 times the thickness, and wherein the length is at least 100 times greater than the width,

wherein the ribbon has fewer than 10 pin holes having a cross-sectional area of at least a square micrometer per square millimeter of surface on average over full surfaces thereof, and

wherein the ceramic grains are lithium garnet.

36. The ribbon of claim **35**, wherein the width is at least 5 mm and no greater than 20 cm.

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