(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
27 August 2015 (27.08.2015)

WIPO | PCT

(10) International Publication Number
WO 2015/127483 A2

(51) International Patent Classification:
C03C 21/00 (2006.01)

(21) International Application Number:
PCT/US2015/023507

(22) International Filing Date:
31 March 2015 (31.03.2015)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/943,758 24 February 2014 (24.02.2014) US

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *without international search report and to be republished upon receipt of that report (Rule 48.2(g))*

[Continued on next page]

(54) Title: STRENGTHENED GLASS ARTICLES HAVING IMPROVED SURVIVABILITY

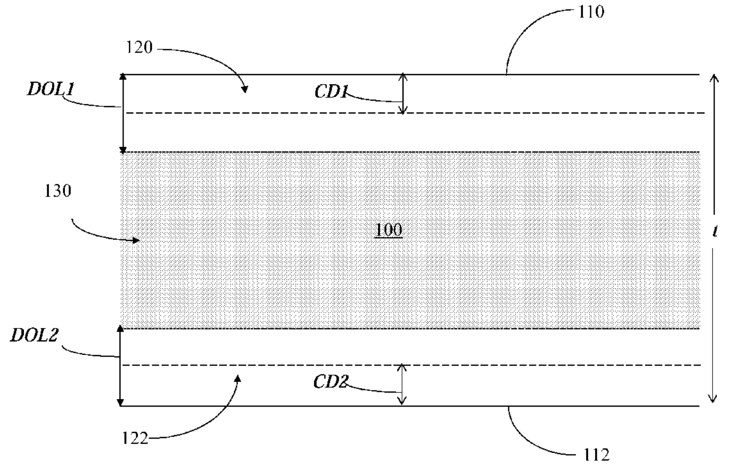

FIG. 1

(57) Abstract: Embodiments are directed to strengthened glass articles comprising a thickness t ≤1 mm (1000 μm), an inner region under a central tension CT (in MPa), and at least one compressive stress layer adjacent the inner region and extending within the strengthened glass article from a surface of the strengthened glass article to a depth of layer DOL (in μm), wherein the strengthened glass article is under a compressive stress at the surface CSS (in MPa), wherein the strengthened glass article is an alkali alumino-silicate glass article comprising 0-5 mol% Li_2O, and at least 3 mol % Al_2O_3, and wherein the DOL ≥ 90 μm, and a CS_s/DOL ratio ≥ 2.5 MPa/μm.

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STRENGTHENED GLASS ARTICLES HAVING IMPROVED SURVIVABILITY

[0001] This application claims the benefit of priority under 35 U.S.C. of U.S Provisional Application Serial No. 61/943758, filed on February 24, 2014, the content of which is relied upon and incorporated herein by reference in its entirety.

BACKGROUND

[0002] Embodiments of the present disclosure are generally directed to strengthened glass having improved fracture resistance, and are specifically directed to fracture resistance strengthened glasses having a compression layer with a depth (DOL) of at least 90 µm.

[0003] Strengthened glasses have been identified for use in electronic devices as well as in other applications. As strengthened glasses are increasingly being utilized, it has become more important to develop strengthened glass materials having improved survivability, especially when subjected to tensile stresses caused by contact with hard/sharp surfaces, such as asphalt or concrete, experienced in “real world” use and applications.

SUMMARY

[0004] Strengthened glasses may be used as cover plates or windows for portable or mobile electronic communication and entertainment devices, such as cellular phones, smart phones, tablets, video players, information terminal (IT) devices, laptop computers and the like. As used herein, the term “cover plate” or “cover glass” includes windows or the like for display and touch screen applications, as well as in other applications requiring transparency, high strength and abrasion resistance. Additionally, the cover glass may be used as used as decorative pieces such as the back and side surfaces of electronic devices.

[0005] To evaluate the strength and abrasion resistance for electronic device cover glass performance, diverse drop test methodologies are used by manufacturers, customers and other market entities. Concrete and asphalt are two typical drop surfaces used when investigating failure probability as a result of sharp contact damage. In such failures, a glass panel including the cover glass may fracture due the glass contacting sharp or hard drop surfaces.

[0006] Embodiments of the disclosure are directed to strengthened glass articles which do not fracture when contacting sharp or hard drop surfaces. Further embodiments of the present disclosure are directed to test methods developed to consistently simulate conditions (e.g., a device dropping on asphalt or concrete) that generate field failures in mobile electronic devices. In specific embodiments of the present disclosure, the test methods use abrasive media of controlled size and chemistry bonded to a surface (e.g. sandpaper) to simulate hard/sharp surface contact, while incrementally increasing the drop height for successive drop tests.

[0007] According to one aspect of the disclosure, a strengthened glass article is provided. The strengthened glass article comprises a thickness $t \leq 1$ mm (1000 μm), an inner region under a central tension CT (in MPa), and at least one compressive stress layer adjacent the inner region and extending within the strengthened glass article from a surface of the strengthened glass article to a depth of layer DOL (in μm), wherein the strengthened glass article is under a compressive stress at the surface CS_s (in MPa). The strengthened glass article is an alkali aluminosilicate glass article comprising 0-5 mol% Li_2O, and at least 3 mol % Al_2O_3. Further, the strengthened glass article has a DOL ≥ 90 μm, and a CS_s/DOL ratio ≥ 2.5 MPa/μm. These CS_s and DOL values were computed using the FSM technique as described below.

[0008] In a further aspect, the strengthened glass article comprises at least 5 mol% Na_2O, and when subjected to a point impact sufficient to break the strengthened glass article, has a frangibility index of less than 3.

[0009] According to yet another aspect, the strengthened glass article comprises a CS_s/DOL ratio ≥ 3.0 MPa/μm, and a CT ≤ 150 MPa.

[0010] These and other aspects, advantages, and salient features will become apparent from the following detailed description, the drawings, and the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] FIG. 1 is a schematic illustration of a strengthened glass article according to one or more embodiments of the present disclosure.

[0012] FIG. 2 is a micrograph showing a flaw on a surface of a strengthened glass article.

[0013] FIGS. 3A is a schematic illustration depicting the impact of flaws for strengthened glass articles with lower DOL compressive layers.

[0014] FIG. 3B is a schematic illustration depicting the impact of flaws for strengthened glass articles with deeper DOL compressive layers.

[0015] FIG. 4 is a graphical illustration (“check depth plot”) depicting the comparative effect of flaws for strengthened glass articles with DOL values of 15 µm and 45 µm, respectively.

[0016] FIG. 5 is a graphical illustration of the stress profile of a 1 mm thick strengthened glass having a compressive stress at the surface CS_s of 901 MPa and a DOL of 40 µm.

[0017] FIG. 6 is a graphical illustration of the stress profile of a 1 mm thick strengthened glass having a CS_s of 897 MPa and a DOL of 108 µm according to one or more embodiments of the present disclosure.

[0018] FIG. 7 is a graphical illustration of the stress profile of a 1 mm thick strengthened glass having a CS_s of 225 MPa and a DOL of 112 µm according to one or more embodiments of the present disclosure.

[0019] FIG. 8 is a graphical illustration depicting an exemplary double ion exchange stress profile according to one or more embodiments of the present disclosure.

[0020] FIG. 9 is a graphical illustration which illustrates the drop height failure for strengthened glass articles having various DOL values according to one or more embodiments of the present disclosure

[0021] FIG. 10a is a photograph showing strengthened glass articles 1) exhibiting frangible behavior upon fragmentation; and 2) exhibiting non-frangible behavior upon fragmentation; and

[0022] FIG. 10b is a photograph showing strengthened glass sheets that exhibit non-frangible behavior upon fragmentation.

DETAILED DESCRIPTION

[0023] Embodiments of strengthened glass articles with improved survivability are provided below. The strengthened glass article of the present disclosure, which is typically chemically strengthened via ion exchange but also may be strengthened via lamination or thermal tempering, encompasses various glass types, e.g., aluminosilicate glass (e.g., alkali aluminosilicate glass), soda-lime glass, borosilicate glasses, etc. For example, and not by way of limitation, the glass article is comprised of an alkali aluminosilicate glass.

[0024] A cross-sectional schematic view of a chemically strengthened glass article embodiment is shown in FIG. 1. Glass article 100 has a thickness **t**, first surface 110, and second surface 112. While the embodiment shown in FIG. 1 depicts a glass article 100 as a flat planar sheet or plate, glass article may have other configurations, such as three dimensional shapes or non-planar configurations. Glass article 100 has a first compressive layer 120 extending from first surface 110 to a depth of layer DOL_1 into the bulk of the glass article 100. In the embodiment shown in FIG. 1, glass article 100 also has a second compressive layer 122 extending from second surface 112 to a second depth of layer DOL_2. Glass article 100 also has a central region 130 between compressive layers 120 and 122. Central region 130 is under a tensile stress or central tension (CT), which balances or counteracts the compressive stresses of layers 120 and 122, respectively. As will be explained below, the glass article 100 includes intermediate critical depths CD_1 and CD_2 within compressive stress layers 120 and 122. Without being bound by theory, these intermediate critical depths CD_1 and CD_2 and the compressive stresses at these critical depths are sufficient to increase survivability of the glass article 100 by enveloping or encasing a flaw introduced by sharp impact to first and second surfaces 110, 112 of the glass article 100. For reference, a depiction of a flaw contacting a glass surface is shown in the micrograph of FIG. 2.

[0025] Conventional strengthened glass used for cover applications has depth of layer (DOL) < 50 μm, which is often limited by the capability of the glass to achieve high DOL in a practical ion-exchange time. Without being bound by theory, strengthened glass is strong in compression, and weak in tension. Referring to FIG. 3B, if a flaw 250 is present on the glass surface, provided the flaw 150 is within the compression layer 220 defined by a depth of layer DOL and does not penetrate into the central region 230, the glass will likely not fail. However, referring to FIG. 3A, if the flaw 250 penetrates the compression layer 222 into the central region 232, then the glass can fail. As the DOL of the compression layer 222 is increased in the glass, the glass is able to contain or envelop deeper flaws within the compression layer 222, as illustrated in FIG. 3B.

[0026] For example, FIG. 4 shows the depths of typical flaws in strengthened glass that have failed in the field. As used herein, “failed in the field” means cover glass failures resulting from real world users dropping their commercial smartphone or electronic devices. The data shows that for glass where the DOL is about 15 μm, the typical flaws, which have caused failures, are greater than 15 μm. Likewise, for glass with a depth of layer of 45 μm, typical failure-causing flaws are greater than 45 μm. When viewing the field data of FIG. 4, it is clear that a strengthened glass article with a depth of layer of 15 μm has significantly more failures than a strengthened glass article with a depth of layer of 45 μm, because the deeper DOL is superior at enveloping flaws.

Thus, without being bound theory, strengthened glass articles with a deeper DOL compressive layer improve device survivability in the field due to the ability of the glass to envelop or encase deeper flaws within the compression layer.

[0027] The degree of chemical strengthening achieved by ion exchange may be quantified based on the parameters of central tension (CT), compressive stress (CS), and depth of layer (DOL). Compressive stress CS may be measured near the surface or within the strengthened glass at various depths. The maximum compressive stress value is the measured compressive stress at the surface (CS_s) of the strengthened glass. The ion exchange process yields a compressive stress layer having a thickness defined as a depth of layer (DOL). The central tension CT, which is computed for the inner region adjacent the compressive stress layer within a glass article, can be calculated from the compressive stress CS, the thickness t, and the DOL.

[0028] Compressive stress and depth of layer are measured using those means known in the art. Such means include, but are not limited to, measurement of surface stress (FSM) using commercially available instruments such as the FSM-6000, manufactured by Luceo Co., Ltd. (Tokyo, Japan), or the like, and methods of measuring compressive stress and depth of layer are described in ASTM 1422C-99, entitled “Standard Specification for Chemically Strengthened Flat Glass,” and ASTM 1279.19779 “Standard Test Method for Non-Destructive Photoelastic Measurement of Edge and Surface Stresses in Annealed, Heat-Strengthened, and Fully-Tempered Flat Glass,” the contents of which are incorporated herein by reference in their entirety. Surface stress measurements rely upon the accurate measurement of the stress optical coefficient (SOC), which is related to the birefringence of the glass. SOC in turn is measured by those methods that are known in the art, such as fiber and four point bend methods, both of which are described in ASTM standard C770-98 (2008), entitled “Standard Test Method for Measurement of Glass Stress-Optical Coefficient,” the contents of which are incorporated herein by reference in their entirety, and a bulk cylinder method. In various sections of the disclosure, central tension CT and compressive stress CS are expressed herein in megaPascals (MPa), thickness **t** is expressed in either microns (μm) or millimeters (mm) and depth of layer DOL is expressed in microns (μm).

[0029] The DOL values disclosed herein, specifically the DOL values of at least 90 μm, reflect DOL values computed using the FSM technique. For clarity, the DOL value represents the thickness of at least one compression stress layers, which means that the strengthened glass article may have one compression layer with a DOL of at least 90 μm or two compression layers with each having a DOL of at least 90 μm. The disclosed DOL values are not a combination, for example, a sum or average, of the two compressive stress layers.

[0030] While the DOL values disclosed and claimed herein were obtained using the FSM technique; however, for illustration purposes only, the stress profiles of FIGS. 5-8 were plotted using the Roussev technique. The Roussev technique is described in the Roussev et al U.S. Application Serial No. US 13/463,322 entitled *Systems And Methods for Measuring the Stress Profile of Ion-Exchanged Glass*, which is incorporated by reference herein in its entirety, discloses two methods for extracting detailed and precise stress profiles (stress as a function of depth) of tempered or chemically strengthened glass.

[0031] In accordance with one embodiment of the present disclosure, the strengthened glass article is an alkali aluminosilicate glass article comprising a thickness $t \leq 1$ mm (1000 μm), a DOL ≥ 90 μm, and a CS_s/DOL ratio ≥ 2.5 MPa/μm.

[0032] The numerous exemplary glass compositions provided below demonstrate that various glass compositions are suitable; however, in specific embodiments, the alkali aluminosilicate glass may comprise 0-5 mol% Li_2O, or 0-1 mol% Li_2O. Alternatively, the strengthened glass article may comprise at least 3 mol% Al_2O_3, or about 3-17 mol% Al_2O_3. In further exemplary embodiments, the alkali aluminosilicate glass may comprise 0-5 mol% K_2O, and/or 0-10 mol% MgO. Moreover, the alkali aluminosilicate may also comprise at least 5 mol % Na_2O, or at least 8 mol% Na_2O, or at least 12 mol% Na_2O. Alternative glass embodiments may include a range of 5-20 mol% Na_2O

[0033] Moreover, various DOL values are contemplated for the deep DOL glass articles of the present disclosure, for example, DOL values of at least 90 μm as stated above, or at least 100 μm, or at least 110 μm. In further embodiments, the DOL may be in a range from 90 to 150 μm, or from 90 to 120 μm. Without being limited by theory, strengthened glass articles having this deeper DOL exhibit fracture resistance even when formed into 3D shapes.

[0034] For strengthened glasses with these deeper DOL values (i.e., ≥ 90 μm), various compressive stress values at the surface, CS_s, are contemplated. For example and not by way of limitation, the strengthened glass may include a CS_s of at least 250 MPa, or at least 300 MPa, or at least 350 MPa. In further embodiments, the strengthened glasses may have a CS_s in a range from 350 to 500 MPa, or at least 500 MPa. Moreover, the strengthened glass article may also exhibit higher compressive stress values, for example, in a range from 700 to 1200 MPa, or from 800 to 1000 MPa.

[0035] As stated above, the strengthened glass articles may exhibit a CS_s/DOL ratio ≥ 2.5 MPa; however, various ratios are contemplated. For example, the strengthened glass articles may include a CS_s/DOL ratio ≥ 3.0 MPa. Moreover, the CS_s/DOL ratio may be defined by a range of 2.5 MPa/μm ≤ CS_s/DOL ≤ 15 MPa/μm, or 3 MPa/μm ≤ CS_s/DOL ≤ 12 MPa/μm. For a lower CS_s glass, the CS/DOL ratio may be in a range of 3 MPa/μm ≤ CS/DOL ≤ 5 MPa/μm. Alternatively, for a higher CS_s glass, the CS/DOL ratio may be in a range of 8 MPa/μm/ ≤ CS/DOL ≤ 10 MPa/μm.

[0036] As the strengthened glasses of the present disclosure are considered suitable for various shapes (e.g., 2D and 3D shapes) and may be utilized in various applications, various thicknesses are contemplated herein. In cover glass applications, the strengthened glass articles may comprise a thickness t ≤ 1.0 mm. In another embodiment, the strengthened glass article may have a thickness t ≤ 0.9 mm. In further embodiments, the thickness of the glass article is in a range from about 0.1 mm up to about 1.0 mm, or from about 0.2 mm to about 0.9 mm, or from about 0.5 to about 0.8 mm. In yet another embodiment, the glass may comprise a thickness in a range from about 0.3 mm to about 0.5 mm.

[0037] Furthermore, the deep DOL strengthened glass articles may be defined by a ratio of the DOL to the thickness of the glass. For example, the relationship of DOL to the thickness t may be defined by the following equation: $0.2t \geq DOL \geq 0.1t$. In a specific embodiment, the strengthened glass article may be defined by the following equation $0.12t \geq DOL \geq 0.1t$.

[0038] As stated above, strengthened glass articles also may be defined by its central tension. In one or more embodiments of the present disclosure, the strengthened glass article has a $CT \leq 150$ MPa, or a $CT \leq 125$ MPa, or $CT \leq 100$ MPa. The central tension of the strengthened glass correlates to the frangible behavior of the strengthened glass article.

[0039] Frangible behavior is characterized by at least one of: breaking of the strengthened glass article (e.g., a plate or sheet) into multiple small pieces (e.g., ≤ 1 mm); the number of fragments formed per unit area of the glass article; multiple crack branching from an initial crack in the glass article; violent ejection of at least one fragment a specified distance (e.g., about 5 cm, or about 2 inches) from its original location; and combinations of any of the foregoing breaking (size and density), cracking, and ejecting behaviors. As used herein, the terms “frangible behavior” and “frangibility” refer to those modes of violent or energetic fragmentation of a strengthened glass article absent any external restraints, such as coatings, adhesive layers, or the like. While coatings, adhesive layers, and the like may be used in conjunction with the strengthened glass articles described herein, such external restraints are not used in determining the frangibility or frangible behavior of the glass articles.

[0040] FIGS. 10a and 10b illustrate examples of frangible behavior and non-frangible behavior of strengthened glass articles upon point impact with a sharp indenter. The point impact test that is used to determine frangible behavior includes an apparatus that is delivered to the surface of the glass article with a force that is just sufficient to release the internally stored energy present within the strengthened glass article. That is, the point impact force is sufficient to create at least one new crack at the surface of the strengthened glass sheet and extend the crack through the compressive stress CS region (i.e., depth of layer) into the region that is under central tension CT. The impact energy needed to create or activate the crack in a strengthened glass sheet depends upon the compressive stress CS and depth of layer DOL of the article, and thus upon the conditions under which the sheet was strengthened (i.e., the conditions used to strengthen a glass by ion exchange). Otherwise, each ion exchanged glass plate shown in FIGS. 10a and 10b was subjected to a sharp dart indenter contact sufficient to propagate a crack into the inner region of the plate, the inner region being under tensile stress. The force applied to the glass plate was just sufficient to reach the beginning of the inner region, thus allowing the energy that drives the crack to come from the tensile stresses in the inner region rather than from the force of the dart impact on the outer surface.

[0041] Referring to FIG. 10a, glass plate **a** can be classified as being frangible. In particular, glass plate **a** fragmented into multiple small pieces that were ejected, and exhibited a large degree of crack branching from the initial crack to produce the small pieces. Approximately 50% of the fragments are less than 1mm in size, and it is estimated that about 8 to 10 cracks branched from the initial crack. Glass pieces were also ejected about 5 cm from original glass plate **a**, as seen in FIG. 10a. A glass article that exhibits any of the three criteria (i.e., multiple crack branching, ejection, and extreme fragmentation) described hereinabove is classified as being frangible. For example, if a glass exhibits excessive branching alone but does not exhibit ejection or extreme fragmentation as described above, the glass is still characterized as frangible.

[0042] Glass plates **b**, **c**, (FIG. 10b) and **d** (FIG. 10a) are classified as not frangible. In each of these samples, the glass sheet has broken into a small number of large pieces. Glass plate **b** (FIG. 10b), for example, has broken into two large pieces with no crack branching; glass plate **c** (FIG. 10b) has broken into four pieces with two cracks branching from the initial crack; and glass plate **d** (FIG. 10a) has broken into four pieces with two cracks branching from the initial crack. Based on the absence of ejected fragments (i.e., no glass pieces forcefully ejected more than 2 inches from their original location), no visible fragments ≤ 1mm in size, and the minimal amount of observed crack branching, samples **b**, **c**, and **d** are classified as non-frangible or substantially non-frangible.

[0043] Based on the foregoing, a frangibility index (Table 1) can be constructed to quantify the degree of frangible or non-frangible behavior of a glass, glass ceramic, and/or a ceramic article upon impact with another object. Index numbers, ranging from 1 for non-frangible behavior to 5 for highly frangible behavior, have been assigned to describe different levels of frangibility or non-frangibility. Using the index, frangibility can be characterized in terms of numerous parameters: 1) the percentage of the population of fragments having a diameter (i.e., maximum dimension) of less than 1 mm ("Fragment size" in Table 1); 2) the number of fragments formed per unit area (in this instance, cm^2) of the sample ("Fragment density" in Table 1); 3) the number of cracks branching from the initial crack formed upon impact ("Crack branching" in Table 1); and 4) the percentage of the population of fragments that is ejected upon impact more than about 5 cm (or about 2 inches) from their original position ("Ejection" in Table 1).

[0044] Table 1. Criteria for determining the degree of frangibility and frangibility index.

Degree of frangibility	**Frangibility index**	**Fragment size (%≤ 1 mm)**	**Fragment density (fragments/cm^2)**	**Crack branching**	**Ejection (% ≥ 5 cm)**
High	5	> 20	>7	> 9	>6
Medium	4	$10 < n \leq 20$	$5 < n \leq 7$	$7 < n \leq 9$	$4< n \leq 6$
Low	3	$5 < n \leq 10$	$3 < n \leq 5$	$5 < n \leq 7$	$2 < n \leq 4$
None	2	$0 < n \leq 5$	$1< n \leq 3$	$2 < n \leq 5$	$0 < n \leq 2$
	1	0	$n \leq 1$	$n \leq 2$	0

[0045] A frangibility index is assigned to a glass article if the article meets at least one of the criteria associated with a particular index value. Alternatively, if a glass article meets criteria between two particular levels of frangibility, the article may be assigned a frangibility index range (e.g., a frangibility index of 2-3). The glass article may be assigned the highest value of frangibility index, as determined from the individual criteria listed in Table 1. In many instances, it is not possible to ascertain the values of each of the criteria, such as the fragmentation density or percentage of fragments ejected more than 5 cm from their original position, listed in Table 1. The different criteria are thus considered individual, alternative measures of frangible behavior and the frangibility index such that a glass article falling within one criteria level will be assigned the corresponding degree of frangibility and frangibility index. If the frangibility index based on any of the four criteria listed in Table 1 is 3 or greater, the glass article is classified as frangible.

[0046] Applying the foregoing frangibility index to the samples shown in FIGS. 10a and 10b, glass plate **a** fragmented into multiple ejected small pieces and exhibited a large degree of crack branching from the initial crack to produce the small pieces. Approximately 50% of the fragments are less than 1 mm in size and it is estimated that about 8 to 10 cracks branched from the initial crack. Based upon the criteria listed in Table 1, glass plate **a** has a frangibility index of between about 4-5, and is classified as having a medium-high degree of frangibility.

[0047] A glass article having a frangibility index of less than 3 (low frangibility) may be considered to be non-frangible or substantially non-frangible. Glass plates **b**, **c**, and **d** each lack fragments having a diameter of less than 1 mm, multiple branching from the initial crack formed upon impact and fragments ejected more than 5 cm from their original position. Glass plates **b**, **c**, and **d** are non-frangible and thus have a frangibility index of 1 (not frangible).

[0048] As previously discussed, the observed differences in behavior between glass plate **a**, which exhibited frangible behavior, and glass plates **b, c,** and **d**, which exhibited non-frangible behavior, in FIGS. 10a and 10b can be attributed to differences in central tension CT among the samples tested. The possibility of such frangible behavior is one consideration in designing various glass products, such as cover plates or windows for portable or mobile electronic devices such as cellular phones, entertainment devices, and the like, as well as for displays for information terminal (IT) devices, such as laptop computers. Moreover, the depth of the compression layer DOL and the maximum value of compressive stress CS_s that can be designed into or provided to a glass article are limited by such frangible behavior.

[0049] Accordingly, in further embodiments of the present disclosure, the strengthened glass article, when subjected to a point impact sufficient to break the strengthened glass article, has a frangibility index of less than 3. Further embodiments of non-frangible strengthened glass articles may achieve a frangibility index less than 2 or less than 1.

[0050] Further elaborating on the discussion of intermediate critical depths above, the strengthened glass articles of the present disclosure may have a stress profile such that the compressive stress CS_D at an intermediate critical depth of 50 µm below the surface of the strengthened glass article is at least 50 MPa. Additionally, other intermediate critical depths (CD, in µm) below the surface of the glass are also suitable if they have a compressive stress sufficient to envelop or encompass a flaw, thereby preventing fracture or failure of the glass. For example and not by way of limitation, the CD may be in a range from 40 to 60 µm, or about 50 µm. In exemplary embodiments, the compressive stress (CS_D) at the CD exhibits a CS_D/CD value ≥ 0.5, or in a range from 1 to 5, or from 1 to 3. In further embodiments, at a CD value of 50 µm, the CS_D is at least 50 MPa, or at least 70 MPa, or in a range from 70 to 200 MPa. Alternatively, it is contemplated that the CS_D at the CD may also be less than 50 MPa, for example, in a range from 5 to 50 MPa. Additionally, the stress profile of the strengthened glass may be defined by a CS_D at a depth of 50 µm of least 10% of CS_s, or at least 25% of CS_s, or in a range from 25 to 75% of CS_s.

[0051] Without being bound by theory, the strengthened glass articles of the present disclosure demonstrate improved fracture resistance when subjected to repeated drop tests. While the person of ordinary skill in the art may contemplate various experimental parameters for the drop test, the strengthened glass articles of the present disclosure are able to withstand fracture when dropped in a drop test from a height of at least 100 cm onto a drop surface, or from a height of at least 150 cm, or from a height of at least 200 cm, or from a height of 220 cm.

[0052] Further demonstrating the improved survivability of the strengthened glass, the strengthened glass is able to withstand fracture when the strengthened glass contacts the drop surface at a flat angle, at a non-flat angle, or both. As used herein, “flat angle” means 180° relative to the drop surface. Various angles relative to the drop surface are contemplated for the “non-flat angle”. In the examples below, the non-flat angle is 30° relative to the drop surface.

[0053] In accordance with the present disclosure, the drop surface is an abrasive surface configured to simulate damage that may result when an electronic device is dropped on “real world” surfaces, such as asphalt. Surviving repeated drops onto the abrasive surface is an indication of better performance on asphalt, as well as other surfaces, e.g., concrete or granite. Various materials are contemplated for the abrasive surface. In a specific embodiment, the abrasive surface is sandpaper, such as SiC sandpaper, engineered sandpaper, or any abrasive material having comparable hardness and/or sharpness that is known to one of ordinary skill in the art. In the experimental examples shown below, SiC sandpaper comprising 180 grit and an average particle size of about 80 μm was used, because it has a known range of particle sharpness, a surface topography more consistent than concrete or asphalt, and a particle size and sharpness that produces the desired level of specimen surface damage. One non-limiting example of commercially available 180 grit SiC sandpaper that may be used in the drop tests described herein is Rhynowet® 180 grit SiC sandpaper produced by Indasa.

[0054] In the tests, the sandpaper may be replaced after each drop to avoid “aging” effects that have been observed in repeated use of concrete or asphalt drop surfaces. In addition to aging, different asphalt morphologies and/or different temperatures and humidity may affect the performance of asphalt. Unlike concrete or asphalt, the sandpaper abrasive surface delivers a consistent amount of damage across all samples.

[0055] Moreover, in the drop tests (examples of which are provided below), various drop heights are utilized. For example, the drop test may utilize a minimum drop height to start (for example, a drop height of about 10-20 cm in the examples below), and may increase the height by set or variable increments for successive drops. Once the strengthened glass breaks, the test is stopped. Alternatively, if the drop height reaches the maximum drop height (for example, a height of about 220 cm in the examples below), and the glass is not fractured upon dropping, the drop test may also be stopped, or the strengthened glass article may be repeatedly dropped from that maximum height.

[0056] In addition to the compositional embodiments listed above, the alkali aluminosilicate glass may encompass various glass compositions as listed below.

[0057] In one embodiment, the alkali aluminosilicate glass comprises: at least one of alumina and boron oxide, and at least one of an alkali metal oxide and an alkali earth metal oxide, wherein $-15 \text{ mol\%} \leq (R_2O + R'O - Al_2O_3 - ZrO_2) - B_2O_3 \leq 4 \text{ mol\%}$, where R is one of Li, Na, K, Rb, and Cs, and R′ is one of Mg, Ca, Sr, and Ba. In some embodiments, the alkali aluminosilicate glass comprises: from about 62 mol% to about 70 mol.% SiO_2; from 0 mol% to about 18 mol% Al_2O_3; from 0 mol% to about 10 mol% B_2O_3; from 0mol% to about 15 mol% Li_2O; from 0 mol% to about 20 mol% Na_2O; from 0 mol% to about 18 mol% K_2O; from 0 mol% to about17 mol% MgO; from 0 mol% to about18 mol% CaO; and from 0 mol% to about5 mol% ZrO_2. The glass is described in U.S. Patent Application No. 12/277,573 by Matthew J. Dejneka et al., entitled “Glasses Having Improved Toughness and Scratch Resistance,” filed November 25, 2008, and claiming priority to U.S. Provisional Patent Application No. 61/004,677, filed on November 29, 2007, the contents of which are incorporated herein by reference in their entirety.

[0058] In another embodiment, the alkali aluminosilicate glass comprises: from about 60 mol% to about 70 mol% SiO_2; from about 6 mol% to about 14 mol% Al_2O_3; from 0 mol% to about 15 mol% B_2O_3; from 0 mol% to about 15 mol% Li_2O; from 0 mol% to about 20 mol% Na_2O; from 0 mol% to about 10 mol% K_2O; from 0 mol% to about 8 mol% MgO; from 0 mol% to about 10 mol% CaO; from 0 mol% to about 5 mol% ZrO_2; from 0 mol% to about 1 mol% SnO_2; from 0 mol% to about 1 mol% CeO_2; less than about 50 ppm As_2O_3; and less than about 50 ppm Sb_2O_3; wherein 12 mol% $\leq Li_2O + Na_2O + K_2O \leq$ 20 mol% and 0 mol% $\leq$ MgO + CaO $\leq$ 10 mol%. The glass is described in U.S. Patent No. 8,158,543 by Sinue Gomez et al., entitled “Fining Agents for Silicate Glasses,” issued on February April 17, 2012, and claiming priority to U.S. Provisional Patent Application No. 61/067,130, filed on February 26, 2008, the contents of which are incorporated herein by reference in their entirety.

[0059] In another embodiment, the alkali aluminosilicate glass has a seed concentration of less than about 1 seed/cm^3 and comprises: 60-72 mol% SiO_2; 6-14 mol% Al_2O_3; 0-15 mol% B_2O_3; 0-1 mol% Li_2O; 0-20 mol% Na_2O; 0-10 mol% K_2O; 0-2.5 mol% CaO; 0-5 mol% ZrO_2; 0-1 mol% SnO_2; and 0-1 mol% CeO_2, wherein 12 mol% $\leq Li_2O + Na_2O + K_2O \leq$ 20 mol%, and wherein the silicate glass comprises less than 50 ppm As_2O_3. In other embodiments, the silicate glass comprises: 60-72 mol% SiO_2; 6-14 mol% Al_2O_3; 0.63-15 mol% B_2O_3; 0-1 mol% Li_2O; 0-20 mol% Na_2O; 0-10 mol% K_2O; 0-10 mol% CaO; 0-5 mol% ZrO_2; 0-1 mol% SnO_2; and 0-1 mol% CeO_2, wherein 12 mol% $\leq Li_2O + Na_2O + K_2O \leq$ 20 mol%. In further embodiments, the silicate glass comprises: 60-72 mol% SiO_2; 6-14 mol% Al_2O_3; 0-15 mol% B_2O_3; 0-1 mol% Li_2O; 0-20 mol% Na_2O; 0-10 mol% K_2O; 0-10 mol% CaO; 0-5 mol% ZrO_2; 0-1 mol% SnO_2; and 0-1 mol% CeO_2, wherein 12 mol% $\leq Li_2O + Na_2O + K_2O \leq$ 20 mol%, wherein 0.1 mol% $\leq SnO_2 + CeO_2 \leq$ 2 mol%, and wherein the silicate glass is formed from batch or raw materials that include at least one oxidizer fining agent. The glass is described in U.S. Patent No. 8,431,502 by Sinue Gomez et al., entitled “Silicate Glasses Having Low Seed Concentration,” issued on February April 30, 2013, and claiming priority to U.S.

Provisional Patent Application No. 61/067,130, filed on February 26, 2008, the contents of which are incorporated herein by reference in their entirety.

[0060] In another embodiment, the alkali aluminosilicate glass comprises SiO_2 and Na_2O, wherein the glass has a temperature T_{35kp} at which the glass has a viscosity of 35 kilo poise (kpoise), and wherein the temperature $T_{breakdown}$ at which zircon breaks down to form ZrO_2 and SiO_2 is greater than T_{35kp}. In some embodiments, the alkali aluminosilicate glass comprises: from about 61 mol % to about 75 mol% SiO_2; from about 7 mol % to about 15 mol% Al_2O_3; from 0 mol% to about 12 mol% B_2O_3; from about 9 mol % to about 21 mol% Na_2O; from 0 mol % to about 4 mol% K_2O; from 0 mol% to about 7 mol% MgO; and 0 mol% to about 3 mol% CaO. The glass is described in U.S. Patent Application No. 12/856,840 by Matthew J. Dejneka et al., entitled “Zircon Compatible Glasses for Down Draw,” filed August 10, 2010, and claiming priority to U.S. Provisional Patent Application No. 61/235,762, filed on August 29, 2009, the contents of which are incorporated herein by reference in their entirety.

[0061] In another embodiment, the alkali aluminosilicate glass comprises at least 50 mol% SiO_2 and at least one modifier selected from the group consisting of alkali metal oxides and alkaline earth metal oxides, wherein $[(Al_2O_3\,(mol\%) + B_2O_3(mol\%))/(\sum \text{alkali metal modifiers}\,(mol\%))] > 1$. In some embodiments, the alkali aluminosilicate glass comprises: from 50 mol% to about 72 mol% SiO_2; from about 9 mol% to about 17 mol% Al_2O_3; from about 2 mol% to about 12 mol% B_2O_3; from about 8 mol% to about 16 mol% Na_2O; and from 0 mol% to about 4 mol% K_2O. The glass is described in U.S. Patent Application No. 12/858,490 by Kristen L. Barefoot et al., entitled “Crack And Scratch Resistant Glass and Enclosures Made Therefrom,” filed August 18, 2010, and claiming priority to U.S. Provisional Patent Application No. 61/235,767, filed on August 21, 2009, the contents of which are incorporated herein by reference in their entirety.

[0062] In another embodiment, the alkali aluminosilicate glass comprises SiO_2, Al_2O_3, P_2O_5, and at least one alkali metal oxide (R_2O), wherein $0.75 \leq [(P_2O_5(mol\%) + R_2O(mol\%))/ M_2O_3\,(mol\%)] \leq 1.2$, where $M_2O_3 = Al_2O_3 + B_2O_3$. In some embodiments, the alkali aluminosilicate glass comprises: from about 40 mol% to about 70 mol% SiO_2;

from 0 mol% to about 28 mol% B_2O_3; from 0 mol% to about 28 mol% Al_2O_3; from about 1 mol% to about 14 mol% P_2O_5; and from about 12 mol% to about 16 mol% R_2O; and, in certain embodiments, from about 40 to about 64 mol% SiO_2; from 0 mol% to about 8 mol% B_2O_3; from about 16 mol% to about 28 mol% Al_2O_3; from about 2 mol% to about 12% P_2O_5; and from about 12 mol% to about 16 mol% R_2O. The glass is described in U.S. Patent Application No. 13/305,271 by Dana C. Bookbinder et al., entitled "Ion Exchangeable Glass with Deep Compressive Layer and High Damage Threshold," filed November 28, 2011, and claiming priority to U.S. Provisional Patent Application No. 61/417,941, filed November 30, 2010, the contents of which are incorporated herein by reference in their entirety.

[0063] In still other embodiments, the alkali aluminosilicate glass comprises at least about 4 mol% P_2O_5, wherein $(M_2O_3(\text{mol\%})/R_xO(\text{mol\%})) < 1$, wherein $M_2O_3 = Al_2O_3 + B_2O_3$, and wherein R_xO is the sum of monovalent and divalent cation oxides present in the alkali aluminosilicate glass. In some embodiments, the monovalent and divalent cation oxides are selected from the group consisting of Li_2O, Na_2O, K_2O, Rb_2O, Cs_2O, MgO, CaO, SrO, BaO, and ZnO. In some embodiments, the glass comprises 0 mol% B_2O_3. The glass is described in U.S. Patent Application No. 13/678,013 by Timothy M. Gross, entitled "Ion Exchangeable Glass with High Crack Initiation Threshold," filed November 15, 2012, and claiming priority to U.S. Provisional Patent Application No. 61/560,434 filed November 16, 2011, the contents of which are incorporated herein by reference in their entirety.

[0064] In other embodiments, the alkali aluminosilicate glass comprises at least about 50 mol% SiO_2 and at least about 11 mol% Na_2O, and the compressive stress is at least about 900 MPa. In some embodiments, the glass further comprises Al_2O_3 and at least one of B_2O_3, K_2O, MgO and ZnO, wherein $-340 + 27.1 \cdot Al_2O_3 - 28.7 \cdot B_2O_3 + 15.6 \cdot Na_2O - 61.4 \cdot K_2O + 8.1 \cdot (MgO + ZnO) \geq 0$ mol%. In particular embodiments, the glass comprises: from about 7 mol% to about 26 mol% Al_2O_3; from 0 mol% to about 9 mol% B_2O_3; from about 11 mol% to about 25 mol% Na_2O; from 0 mol% to about 2.5 mol% K_2O; from 0 mol% to about 8.5 mol% MgO; and from 0 mol% to about 1.5 mol%

CaO. The glass is described in U.S. Patent Application No. 13/533,298, by Matthew J. Dejneka et al., entitled “Ion Exchangeable Glass with High Compressive Stress,” filed June 26, 2012, and claiming priority to U.S. Provisional Patent Application No. 61/503,734, filed July 1, 2011, the contents of which are incorporated herein by reference in their entirety.

[0065] In some embodiments, the glass comprises: at least about 50 mol% SiO_2; at least about 10 mol% R_2O, wherein R_2O comprises Na_2O; Al_2O_3; and B_2O_3, wherein $B_2O_3 - (R_2O - Al_2O_3) \geq 3$ mol%. In certain embodiments, the glass comprises: at least about 50 mol% SiO_2; from about 9 mol% to about 22 mol% Al_2O_3; from about 3 mol% to about 10 mol% B_2O_3; from about 9 mol% to about 20 mol% Na_2O; from 0 mol% to about 5 mol% K_2O; at least about 0.1 mol% MgO, ZnO, or combinations thereof, wherein $0 \leq MgO \leq 6$ and $0 \leq ZnO \leq 6$ mol%; and, optionally, at least one of CaO, BaO, and SrO, wherein 0 mol% $\leq$ CaO + SrO + BaO $\leq$ 2 mol%. When ion exchanged, the glass, in some embodiments, has a Vickers crack initiation threshold of at least about 10 kgf. Such glasses are described in U.S. Patent Application No. 13/903,433, by Matthew J. Dejneka et al., entitled “Zircon Compatible, Ion Exchangeable Glass with High Damage Resistance,” filed May 28, 2013, and claiming priority to U.S. Provisional Patent Application No. 61/653,489, filed May 31, 2012, the contents of which are incorporated by reference herein in their entirety.

[0066] In some embodiments, the glass comprises: at least about 50 mol% SiO_2; at least about 10 mol% R_2O, wherein R_2O comprises Na_2O; Al_2O_3, wherein $-0.5 \text{ mol\%} \leq Al_2O_3(\text{mol\%}) - R_2O(\text{mol\%}) \leq 2 \text{ mol\%}$; and B_2O_3, and wherein $B_2O_3(\text{mol\%}) - (R_2O(\text{mol\%}) - Al_2O_3(\text{mol\%})) \geq 4.5$ mol%. In other embodiments, the glass has a zircon breakdown temperature that is equal to the temperature at which the glass has a viscosity of greater than about 40 kPoise and comprises: at least about 50 mol% SiO_2; at least about 10 mol% R_2O, wherein R_2O comprises Na_2O; Al_2O_3; and B_2O_3, wherein $B_2O_3(\text{mol\%}) - (R_2O(\text{mol\%}) - Al_2O_3(\text{mol\%})) \geq 4.5$ mol%. In still other embodiments, the glass is ion exchanged, has a Vickers crack initiation threshold of at least about 30 kgf, and comprises: at least about 50 mol% SiO_2; at least about 10 mol% R_2O, wherein R_2O

comprises Na_2O; Al_2O_3, wherein $-0.5\ \text{mol\%} \leq Al_2O_3(\text{mol\%}) - R_2O(\text{mol\%}) \leq 2\ \text{mol\%}$; and B_2O_3, wherein $B_2O_3(\text{mol\%}) - (R_2O(\text{mol\%}) - Al_2O_3(\text{mol\%})) \geq 4.5\ \text{mol\%}$. Such glasses are described in U.S. Patent Application No. 13/903,398 by Matthew J. Dejneka et al., entitled “Zircon Compatible, Ion Exchangeable Glass with High Damage Resistance,” filed May 28, 2013, and claiming priority to U.S. Provisional Patent Application No. 61/653,485, filed May 31, 2012, the contents of which are incorporated by reference herein in their entirety.

[0067] In some embodiments, the alkali aluminosilicate glasses described hereinabove are substantially free of (i.e., contain 0 mol% of) of at least one of lithium, boron, barium, strontium, bismuth, antimony, and arsenic.

[0068] In addition to those compositions listed above, various other alkali aluminosilicate glass compositions may be used as cover glass in accordance with the present disclosure. Incorporating components and amounts from various embodiments described above is contemplated and considered within the scope of the present disclosure.

[0069] As stated above, the glass articles may be chemically strengthened by ion exchange. In this process, ions in the surface layer of the glass are replaced by – or exchanged with – larger ions having the same valence or oxidation state. In those embodiments in which the glass article comprises, consists essentially of, or consists of an alkali aluminosilicate glass, ions in the surface layer of the glass and the larger ions are monovalent alkali metal cations, such as Li^+ (when present in the glass), Na^+, K^+, Rb^+, and Cs^+. Alternatively, monovalent cations in the surface layer may be replaced with monovalent cations other than alkali metal cations, such as Ag^+ or the like.

[0070] Ion exchange processes are typically carried out by immersing a glass article in a molten salt bath containing the larger ions to be exchanged with the smaller ions in the glass. It will be appreciated by those skilled in the art that parameters for the ion exchange process, including, but not limited to, bath composition and temperature, immersion time, the number of immersions of the glass in a salt bath (or baths), use of multiple salt baths, additional steps such as annealing, washing, and the like, are generally determined by the composition of the glass and the desired depth of layer and compressive stress of the glass that result from the strengthening operation. By way of example, ion exchange of alkali metal-containing glasses may be achieved by immersion in at least one molten bath containing a salt such as, but not limited to, nitrates, sulfates, and chlorides of the larger alkali metal ion. The temperature of the molten salt bath typically is in a range from about 380ºC up to about 450ºC, while immersion times range from about 15 minutes up to about 40 hours. However, temperatures and immersion times different from those described above may also be used.

[0071] In addition, non-limiting examples of ion exchange processes in which glass is immersed in multiple ion exchange baths, with washing and/or annealing steps between immersions, are described in U.S. Patent Application No. 12/500,650, filed July 10, 2009, by Douglas C. Allan et al., entitled "Glass with Compressive Surface for Consumer Applications" and claiming priority from U.S. Provisional Patent Application No. 61/079,995, filed July 11, 2008, in which glass is strengthened by immersion in multiple, successive, ion exchange treatments in salt baths of different concentrations; and U.S. Patent 8,312,739, by Christopher M. Lee et al., issued on November 20, 2012, and entitled "Dual Stage Ion Exchange for Chemical Strengthening of Glass," and claiming priority from U.S. Provisional Patent Application No. 61/084,398, filed July 29, 2008, in which glass is strengthened by ion exchange in a first bath is diluted with an effluent ion, followed by immersion in a second bath having a smaller concentration of the effluent ion than the first bath. The contents of U.S. Patent Application No. 12/500,650 and U.S. Patent No. 8,312,739 are incorporated herein by reference in their entirety. Further, the glass compositions of the present disclosure are down-drawable by processes known in the art, such as slot-drawing, fusion drawing, re-drawing, and the like, and have a liquidus viscosity of at least 130 kilopoise.

[0072] The compressive stress is created by chemically strengthening the glass article, for example, by the ion exchange processes, previously described herein, in which a plurality of first metal ions in the outer region of the glass article is exchanged with a plurality of second metal ions so that the outer region comprises the plurality of the second metal ions. Each of the first metal ions has a first ionic radius and each of the second alkali metal ions has a second ionic radius. The second ionic radius is greater than the first ionic radius, and the presence of the larger second alkali metal ions in the outer region creates the compressive stress in the outer region.

[0073] At least one of the first metal ions and second metal ions are preferably ions of an alkali metal. The first ions may be ions of lithium, sodium, potassium, and rubidium. The second metal ions may be ions of one of sodium, potassium, rubidium, and cesium, with the proviso that the second alkali metal ion has an ionic radius greater than the ionic radius than the first alkali metal ion.

[0074] Referring to the prophetic example of FIG. 8, a strengthened glass article may have a stress profile defined by a first compressive zone (Zone 1) which extends from the surface of the glass to a distance x below the surface, and a second compressive stress zone (Zone 2) extending from the distance x to the DOL. The first compressive zone defines a rate r1 of decrease of compressive stress from the surface to the distance x below the surface, and the second compressive zone defines a rate r2 of decrease of compressive stress from the distance x to the DOL, and $r1 \geq 2r2$. Without being bound by theory, the first compressive stress zone is achieved by an ion exchange step directed to deliver a spike of compressive stress near the surface, whereas the second compressive zone is achieved by a separate ion exchange step directed to deliver a deeper DOL in the glass. As described below, the stress profile of FIG. 6 depicts a stress profile of glass article chemically strengthened via double ion exchange.

[0075] In a further embodiment of the present disclosure, a method of producing a strengthened glass article having a thickness $t \leq 1$mm and at least one compressive stress layer extending from a surface of the strengthened glass article to a depth of layer DOL (in μm) ≥ 90 μm is provided. The method includes a first ion exchange step wherein an alkali aluminosilicate glass article is immersed in a first ion exchange bath at a temperature of greater than 400°C for a time sufficient such that the compressive stress layer has a depth of at least 70 μm after the first ion exchange step.

[0076] While various time periods are contemplated as suitable, the first ion exchange step may be conducted for a time of at least 8 hours. Without being bound by theory, longer ion exchange periods for the first ion exchange step may correlate with larger sodium ion content in the first ion exchange bath. For example and not by way of limitation, the desired sodium ion content in first ion exchange bath may be achieved by including at least about 30% by weight of a sodium composition, or at least about 40% by weight in the first ion exchange bath, or optionally including a range of about 40% to about 60% by weight of the sodium composition in the first ion exchange bath. In an exemplary embodiment, the sodium composition is $NaNO_3$. In a further embodiment, the temperature of the first ion exchange step may be 450°C or greater.

[0077] After the first ion exchange step is performed, the strengthened glass article may have a compressive stress (CS) of at least 150 MPa. In further embodiments, the strengthened glass article may have a CS of at least 200 MPa after the first ion exchange step, or a CS range of about 200 to about 300 MPa after the first ion exchange step. While the first ion exchange step minimally achieves a compressive layer depth of at least 70 μm, it is contemplated that the compressive stress layer may have a depth of 70-85 μm after the first ion exchange step.

[0078] After completion of the first ion exchange step, the second ion exchange step may be conducted by immersing the alkali aluminosilicate glass article in a second ion exchange bath different from the first ion exchange bath at a temperature of at least 350°C for a time sufficient to produce the compressive layer having DOL ≥ 90 μm.

[0079] Without being bound by theory, the second ion exchange step is considered to be a rapid ion exchange step that yields a “spike” of compressive stress near the surface of the glass as depicted in FIG. 8. In one or more embodiments, the second ion exchange step may be conducted for a time of 30 minutes or less, or for a time of 15 minutes or less, or optionally may be conducted in a range of about 10 to about 15 minutes.

[0080] Further without being bound by theory, the second ion exchange bath is different than the first ion exchange bath, because the second ion exchange step is directed to delivering a different ion to the alkali aluminosilicate glass article than the first ion exchange step. In one or more embodiments, the second ion exchange bath may comprise at least about 95% by weight of a potassium composition that delivers potassium ions to the alkali aluminosilicate glass article. In a specific embodiment, the second ion exchange bath may comprise from about 98% to about 99.5% by weight of the potassium composition. While it is possible that the second ion exchange bath only comprises a potassium composition, the second ion exchange bath may, in further embodiments, comprise 0-2% by weight, or about 0.5-1.5% by weight of a sodium composition, for example, $NaNO_3$. In an exemplary embodiment, the potassium composition is KNO_3. In further embodiments, the temperature of the second ion exchange step may be 390°C or greater.

[0081] After the second ion exchange step, which may conclude the chemical strengthening procedure, the strengthened glass article may have a compressive stress (CS) of at least 700 MPa. In a further embodiment, the strengthened glass article has a compressive stress of about 700 to about 1200 MPa, or about 700 to 1000 MPa after the second ion exchange step. While the second ion exchange step minimally achieves a compressive layer DOL of at least 90 μm, it is contemplated that the compressive stress layer may have a DOL in a range of about 90-130 μm after the second ion exchange step.

[0082] For illustration, an exemplary double ion exchange procedure performed on alkali aluminosilicate glass compositions having a thickness of 0.5 mm is provided below. These alkali aluminosilicate glass compositions are disclosed in U.S. Application No. 13/305,271, and are also included in paragraph [0061] above. The first ion exchange step utilized an ion exchange bath comprising 43-52% $NaNO_3$ by weight, and was conducted for a time period greater than 8 hours at a temperature of approximately

450°C. The second exchange step utilized an ion exchange bath comprising 0-1.4% $NaNO_3$ by weight and the remainder being KNO_3. The second ion exchange step was conducted for a period of 11-14 minutes, and 13-14 minutes in specific instances.

[0083] The compression layer depth after this first ion exchange step ranged from about 72 to about 83 microns, and the compressive stress was approximately 215-265 MPa. After both steps of the double ion exchange are performed, the exemplary glass included a DOL range of approximately 100-126 um, and a CS range of about 760 to 960 MPa. In these glass examples, the depth of the stress spike, which is the depth within the glass where the CS value is half of the peak CS at the surface, was about 5.5-7 μm from the surface of the glass article.

[0084] **DROP TEST PROCEDURE**

[0085] The following description lists a detailed procedural framework previously utilized to perform sandpaper drop tests.

[0086] **Drop Tester Equipment**

[0087] For the drop tests, a Yoshida Seiki DT-205 Drop Test System was utilized and was oriented to fully contact but not be secured to a painted concrete floor. The steel base plate was ~¾" thick and stock rectangular polymer jaws with vertical parallel faces were utilized. The test devices were commercially available smartphones retrofitted with the strengthened cover glass of the present disclosure such that the glass sat "proud (i.e., above the bezel and not recessed in the frame of the phone). Drop tests using as-manufactured phones confirmed that the drop tests described above were truly representative of damage incurred in normal use.

[0088] Drop Surface Preparation

[0089] For drop surface preparation, two pieces of 9x11" Rhynowet 180 grit SiC sandpaper were used. A first piece was centered below the drop tester jaws and the back surface was fully adhered to the steel base plate of the drop tester with a thin layer of Scotch Spray Mount™ contact adhesive to prevent lateral movement of the actual drop surface.

[0090] A second piece of sandpaper, the actual drop surface, was aligned to fully cover the above first piece, SiC-side up, without adhesive being used; rather, this piece was held in place with four strong, rare earth magnets in each corner. Each magnet was covered with a polymer fingertip cut from a cut-resistant glove to prevent contact damage to the cover glass if the device bounced to the side. A new second piece of sandpaper was used for each test device; however, the same sheet was used for the entire drop sequence of this one device.

[0091] The test device was loaded into the drop tester jaws with the cover glass facing downward and parallel to the plane of the SiC drop surface. To ensure a smooth release, the jaws did not contact any buttons or other physical phone features that extend beyond the contact surface of the device edges; the jaws only contacted the long edges of the drop test device. The test device edges were aligned to contact the vertical midpoints of the jaws, which were in turn centered on the jaw air piston actuators. This prevented the creation of non-normal forces and protected against created forces that could be imparted to the test device

[0092] The test device was loaded into the drop tester jaws with the cover glass facing downward and parallel to the plane of the SiC drop surface. To ensure a smooth release, the jaws did not contact any buttons or other physical phone features that extend beyond the contact surface of the device edges; the jaws only contacted the long edges of the drop test device. The test device edges were aligned to contact the vertical midpoints of the jaws, which were in turn centered on the jaw air piston actuators. This prevented the creation of non-normal forces and protected against created forces that could be imparted to the test device

[0093] Drop Test

[0094] The first drop was performed at a starting height of 20 cm, which represented the distance from the exposed surface of the cover glass to the top of the drop surface. If no cover glass failure occurred, the drop height was increased by 10 cm, and the device was aligned within the jaws and dropped again. The test device was continually dropped at 10 cm increments until the cover glass failed or until the cover glass survived the maximum drop height of 220 cm.

[0095] For the next device drop, the magnets and the used top piece of SiC sandpaper were removed. The steel drop tester base plate and the bottom first piece of SiC sandpaper were cleaned with a brush and then subjected to compressed air to remove loose contaminants. At which point, the above drop procedure was performed again.

[0096] **EXAMPLES**

[0097] The following examples (Examples 1-3) demonstrate the improved survivability of strengthened alkali aluminosilicate glasses having a DOL ≥ 90 by comparison to shallower DOL glasses conventionally used in cover glass.

[0098] Example 1

[0099] In the comparative examples, the glass used as a basis for the comparison in the control and experimental glasses below had the following composition in wt%: 58.5% SiO_2, 21.51% Al_2O_3, 5.2% B_2O_3, 13.01% Na_2O, 0.02% K_2O, 1.51% MgO, 0.03% CaO, and 0.18% SnO_2.

[00100] As shown in Table 1 below, the control strengthened glass was ion exchanged for 5 hours at 430° in a KNO_3 bath to yield a CS_s = 805 MPa, and a DOL = 40 μm. The experimental strengthened glass was ion exchanged for 27 hours at 450° in a KNO_3 bath to yield a CS_s=376 MPa, and a DOL=97 μm in accordance with the present disclosure. These CS_s and DOL values were computed using FSM. The test method was initially performed beginning at a height of 20 cm and was increased at 10 cm increments for subsequent drops until reaching a maximum height of 220 cm. The drop height for failure was recorded as a metric for both angled drops and flat face drops. The drop surface was a 180 grit SiC sandpaper upper surface disposed on a steel plate. In the tests, the strengthened glass was installed into a commercial smartphone device to best simulate real world dropping conditions. The 30 degree drop and flat (180 degree) drop were oriented with the glass being tested on the device facing the drop surface during impact, so that it was the first surface to make contact with the drop surface.

[00101] Table 1

	Control Strengthened Glass	**Experimental Strengthened Glass**
DOL	40	97
Ion Exchange Time (hrs)	5	27
Ion Exchange Temperature (°C)	430	450
Na concentration in KNO_3 bath (wt %)	2%	29%

[00102] As shown in Table 2 below, strengthened glass with a DOL of 40 μm experienced cover glass fracture at drop heights of 102.5 cm on average for the flat face drop test and 114 cm for the 30° drop tests. However, strengthened glass with a DOL of 97 μm was subjected to 4 drops at 220 cm in the flat face drop tests and 5 drops at 220 cm in the 30° drop tests, and the strengthened glass did not experience cover glass fracture or failure.

[00103] Table 2

	Flat Face Drop	**30 Degree Drop**
DOL	**Avg. Break Height (cm)**	**Avg. Break Height (cm)**

40	102.5	114
97	No Breakage at 220 cm	No Breakage at 220 cm

[00104] Example 2

[00105] Additionally, another drop test experiment was conducted for a strengthened glass having a DOL = 151 using the same procedure as in Example 1. The strengthened glass composition in wt% was approximately: 47.93% SiO_2, 23.31% Al_2O_3, 12.73 P_2O_5, 14.37% Na_2O, 1.56% MgO, and 0.11% SnO_2. The glass was ion exchanged to yield approximately a CS_s=232 MPa, and a DOL=151 μm as computed via FSM. The strengthened glass had a 1 mm thickness and was incorporated into a smartphone device. Upon conducting the same drop testing procedure as in Example 1, the glass survived 5 flat face drops at a 220 cm height, and also survived 5 30° angle drops at a 220 cm height.

[00106] Example 3

[00107] In this example, an exemplary 3D shape glass having a thickness of 0.8 mm, dimensions of 55.9 mm x 121.0 mm, and a bend radius of 3 mm was tested. The glass had a composition in wt% as follows: 61.22% SiO_2, 16.03 wt% Al_2O_3, 0.62% B_2O_3, 13.85% Na_2O, 3.55% K_2O, 3.7% MgO, 0.5% CaO, 0.52% SnO_2, and 0.1% ZrO_2.

[00108] The glass underwent a single ion exchange to yield a CS_s=787 MPa and a DOL=95 μm as computed via FSM. Flat face drop tests were performed starting at a 30 cm drop height with increasing increments of 10 cm up to a max height of 200 cm. The glass was dropped 4 times from a 200 cm height and demonstrated no breakage or fracture.

[00109] Example 4

[00110] As further illustration, FIGS. 6 and 7 show stress profiles of 1 mm thick strengthened alkali aluminosilicate glass article samples having a deeper DOL (i.e., DOL ≥ 90 μm) in contrast to the lower DOL glass sample (DOL = 40 μm) of FIG. 5. As stated above, the stress profile curves were plotted using the Roussev technique.

[00111] FIG. 6 depicts a strengthened glass article having a compressive stress spike on the surface. The strengthened glass article, which has a CS_s of 897 MPa and a DOL of 108 μm, has a compressive stress CS_D of about 100 MPa at a depth of 50 μm. As noted above, FIG. 6 is a double ion exchanged glass article which includes a compressive stress spike near the surface of the glass.

[00112] Unlike FIG. 6, which depicts the stress profile of a double ion exchanged strengthened glass articles with a compressive stress spike at the surface, the strengthened glass article of FIG. 7 is a single ion exchanged glass having a CS_s of 225 MPa and a DOL of 112 μm, and includes a CS_D of about 110 MPa at a CD of 50 μm.

[00113] While typical embodiments have been set forth for the purpose of illustration, the foregoing description should not be deemed to be a limitation on the scope of the disclosure or appended claims.

[00114] For example, processes other than ion exchange may be used to chemically strengthen the glass, and different means of strengthening the glass may be used in combination with each other to achieve compressive stress within the glass. In one alternative embodiment, metal ions, such as silver or the like, may be used instead of – or in combination with – alkali metal ions in the ion exchange process. Accordingly, various modifications, adaptations, and alternatives may occur to one skilled in the art without departing from the spirit and scope of the present disclosure or appended claims.

CLAIMS

1. A strengthened glass article having a thickness t, wherein $t \leq 1$ mm, an inner region under a central tension CT, and at least one compressive stress layer adjacent to the inner region and extending from a surface of the strengthened glass article to a depth of layer DOL within the strengthened glass article, wherein $0.2t \geq DOL \geq 0.1t$; and wherein the strengthened glass article has a stress profile such that a compressive stress CS_D at an intermediate critical depth of 50 μm below the surface of the strengthened glass article is at least 50 MPa.

2. The strengthened glass article of claim 1, wherein the CS_s is greater than 300 MPa.

3. The strengthened glass article of claim 1 or claim 2, wherein the strengthened glass article comprises 0-5 mol% K_2O.

4. The strengthened glass article of any one of the preceding claims, wherein the thickness t is less than or equal to 0.9 mm.

5. The strengthened glass article of any one of the preceding claims, wherein the strengthened glass article comprises 5-20 mol% Na_2O.

6. The strengthened glass article of any one of the preceding claims, wherein the strengthened glass article comprises 0-10 mol% MgO.

7. The strengthened glass article of any one of the preceding claims, wherein the DOL is in a range from 90 to 120 μm.

8. The strengthened glass article of any one of the preceding claims, wherein the CS_s is in a range from 700 to 1200 MPa.

9. The strengthened glass article of any one of the preceding claims, wherein the thickness t is in a range from about 0.5 mm to about 0.8 mm.

10. The strengthened glass article of any one of the preceding claims, wherein the CT ≤ 150 MPa.

11. The strengthened glass article of any one of the preceding claims, wherein the strengthened glass article has a stress profile defined by a first compressive stress zone extending from the surface of the strengthened glass article to a distance x below the surface, and a second compressive stress zone extending from the distance x to the DOL, and wherein the first compressive stress zone defines a rate r_1 of decrease of compressive stress from the surface to the distance x below the surface, the second compressive stress zone defines a rate r_2 of decrease of compressive stress from the distance x to the DOL, and $r_1 \geq 2r_2$.

12. The strengthened glass article of any one of the preceding claims, wherein the $CS_s \geq 350$ MPa.

13. The strengthened glass article of any one of the preceding claims, wherein the strengthened glass article comprises an alkali aluminosilicate glass.

14. The strengthened glass article of claim 13, wherein the alkali aluminosilicate glass comprises at least about 4 mol% P_2O_5, wherein $(M_2O_3(mol\%)/R_xO(mol\%)) < 1$, wherein $M_2O_3 = Al_2O_3 + B_2O_3$, and wherein R_xO is the sum of monovalent and divalent cation oxides present in the alkali aluminosilicate glass.

15. A strengthened glass article having a thickness t, wherein t ≤ 1 mm, an inner region under a central tension CT, and at least one compressive stress layer adjacent to the inner region and extending from a surface of the strengthened glass article to a depth of layer DOL, wherein 0.2t ≥ DOL ≥ 0.1t, wherein the strengthened glass article is under a compressive stress at the surface CS_s, wherein the strengthened glass article is an alkali aluminosilicate glass article comprising 0-5 mol% Li_2O, at least 3 mol % Al_2O_3, and at least 5 mol% Na_2O, and wherein the strengthened glass article, when subjected to a point impact sufficient to break the strengthened glass article, has a frangibility index of less than 3.

16. The strengthened glass article of claim 15, wherein $CS_s > 300$ MPa.

17. The strengthened glass article of claim 15or claim 16, wherein $CS_s \geq 350$ MPa.

18. The strengthened glass article of any one of claims 15-17, wherein $t \leq 0.9$ mm.

19. The strengthened glass article of any one of claims 15-18, wherein the thickness t is in a range from about 0.5 mm to about 0.8 mm.

20. The strengthened glass article of any one of claims 15-19, wherein the strengthened glass article has a stress profile defined by a first compressive stress zone extending from the surface of the strengthened glass article to a distance x below the surface, and a second compressive stress zone extending from the distance x to the DOL, and wherein the first compressive stress zone defines a rate r_1 of decrease of compressive stress from the surface to the distance x below the surface, the second compressive stress zone defines a rate r_2 of decrease of compressive stress from the distance x to the DOL, and $r_1 \geq 2r_2$.

21. The strengthened glass article of any one of claims 15-20, wherein the strengthened glass article has a stress profile such that a compressive stress CS_D at an intermediate critical depth of 50 μm below the surface of the strengthened glass article is at least 50 MPa

22. The strengthened glass article of any one of claims 15-21, wherein the alkali aluminosilicate glass comprises at least about 4 mol% P_2O_5, wherein $(M_2O_3(\text{mol\%})/R_xO(\text{mol\%})) < 1$, wherein $M_2O_3 = Al_2O_3 + B_2O_3$, and wherein R_xO is the sum of monovalent and divalent cation oxides present in the alkali aluminosilicate glass.

23. A strengthened glass article having a thickness t, wherein $t \leq 1$ mm, an inner region under a central tension CT, and at least one compressive stress layer

adjacent to the inner region and extending from a surface of the strengthened glass article to a depth of layer DOL within the strengthened glass article, wherein $0.2t \geq DOL \geq 0.1t$, wherein the strengthened glass article is under a compressive stress at the surface CS_s, wherein the strengthened glass article is an alkali aluminosilicate glass article comprising 0-5 mol% Li_2O, at least 3 mol % Al_2O_3, and at least 5 mol % Na_2O, and wherein the central tension CT is less than or equal to 150 MPa.

24. The strengthened glass article of claim 23, wherein $CS_s > 300$ MPa.

25. The strengthened glass article of claim 23 or claim 22, wherein $CS_s \geq 350$ MPa.

26. 29. The strengthened glass article of any one of claims 23-25, wherein the thickness $t \leq 0.9$ mm.

27. The strengthened glass article of claim 23, wherein the strengthened glass article has a stress profile defined by a first compressive stress zone which extends from the surface of the strengthened glass article to a distance x below the surface, and a second compressive stress zone extending from the distance x to the DOL, and wherein the first compressive stress zone defines a rate r_1 of decrease of compressive stress from the surface to the distance x below the surface, the second compressive stress zone defines a rate r_2 of decrease of compressive stress from the distance x to the DOL, and $r_1 \geq 2r_2$.

28. The strengthened glass article of claim 23, wherein the strengthened glass article has a stress profile such that a compressive stress CS_D at an intermediate critical depth of 50 μm below the surface of the strengthened glass article is at least 50 MPa.

29. The strengthened glass article of claim 23, wherein the alkali aluminosilicate glass comprises at least about 4 mol% P_2O_5, wherein $(M_2O_3(mol\%)/R_xO(mol\%)) < 1$, wherein $M_2O_3 = Al_2O_3 + B_2O_3$, and wherein R_xO is the sum of monovalent and divalent cation oxides present in the alkali aluminosilicate glass.

30. A method of making a strengthened glass article having a thickness t, wherein t ≤ 1mm, and at least one compressive stress layer extending from a surface of the strengthened glass article to a depth of layer DOL, wherein 0.2t ≥ DOL ≥ 0.1t, the method comprising:

conducting a first ion exchange step by immersing an alkali aluminosilicate glass article in a first ion exchange bath at a temperature of greater than 400°C for a time sufficient such that the compressive stress layer has a depth of at least 70 µm after the first ion exchange step; and

conducting a second ion exchange step by immersing the alkali aluminosilicate glass article in a second ion exchange bath different from the first ion exchange bath at a temperature of at least 350°C for a time sufficient to produce the compressive stress layer in which 0.2t ≥ DOL ≥ 0.1t.

31. The method of claim 30, wherein the first ion exchange step is conducted for a time of at least 8 hours.

32. The method of claim 30, wherein the first ion exchange bath comprises at least about 30% by weight of a sodium composition that delivers sodium ions to the alkali aluminosilicate glass article.

33. The method of claim 32, wherein the first ion exchange bath comprises from about 40% to about 60% by weight of the sodium composition.

34. The method of claim 30, wherein the temperature of the first ion exchange step is 450°C or greater.

35. The method of claim 30, wherein the strengthened glass article has a compressive stress (CS) of at least 150 MPa after the first ion exchange step.

36. The method of claim 35, wherein the strengthened glass article has a CS of about 200 to about 300 MPa after the first ion exchange step.

37. The method of claim 30, wherein the second ion exchange step is conducted for a time of 30 minutes or less.

38. The method of claim 37, wherein the second ion exchange step is conducted for a time of about 10 to about 15 minutes.

39. The method of claim 30, wherein the second ion exchange bath comprises at least about 95% by weight of a potassium composition that delivers potassium ions to the alkali aluminosilicate glass article.

40. The method of claim 39, wherein the second ion exchange bath comprises from about 98% to about 99.5% by weight of the potassium composition.

41. The method of claim 39, wherein the second ion exchange bath comprises 0-2% by weight of a sodium composition.

42. The method of claim 30, wherein the temperature of the second ion exchange step is 390°C or greater.

43. The method of claim 30, wherein the strengthened glass article has a compressive stress of at least 700 MPa after the second ion exchange step.

44. The method of claim 43, wherein the strengthened glass article has a compressive stress of about 700 to about 1000 MPa after the second ion exchange step.

45. The method of claim 30, wherein the compressive stress layer has a depth of 70-85 μm after the first ion exchange step.

46. The method of claim 30, wherein the DOL is in a range of 90-130 μm after the second ion exchange step.

47. The method of claim 30, wherein the strengthened glass article after the second ion exchange bath has a stress profile defined by a first compressive stress zone which extends from the surface of the strengthened glass article to a distance x

below the surface, and a second compressive stress zone extending from the distance x to the DOL, and wherein the first compressive stress zone defines a rate r_1 of decrease of compressive stress from the surface to the distance x below the surface, the second compressive stress zone defines a rate r_2 of decrease of compressive stress from the distance x to the DOL, and $r_1 \geq 2r_2$.

48. The method of claim 30, wherein the strengthened glass article after the second ion exchange bath has a stress profile such that a compressive stress CS_D at an intermediate critical depth of 50 μm below the surface of the strengthened glass article is at least 50 MPa

49. The method of claim 30, wherein the strengthened glass article comprises an alkali aluminosilicate glass.

50. The method of claim 49, wherein the alkali aluminosilicate glass comprises at least about 4 mol% P_2O_5, wherein $(M_2O_3(mol\%)/R_xO(mol\%)) < 1$, wherein $M_2O_3 = Al_2O_3 + B_2O_3$, and wherein R_xO is the sum of monovalent and divalent cation oxides present in the alkali aluminosilicate glass.

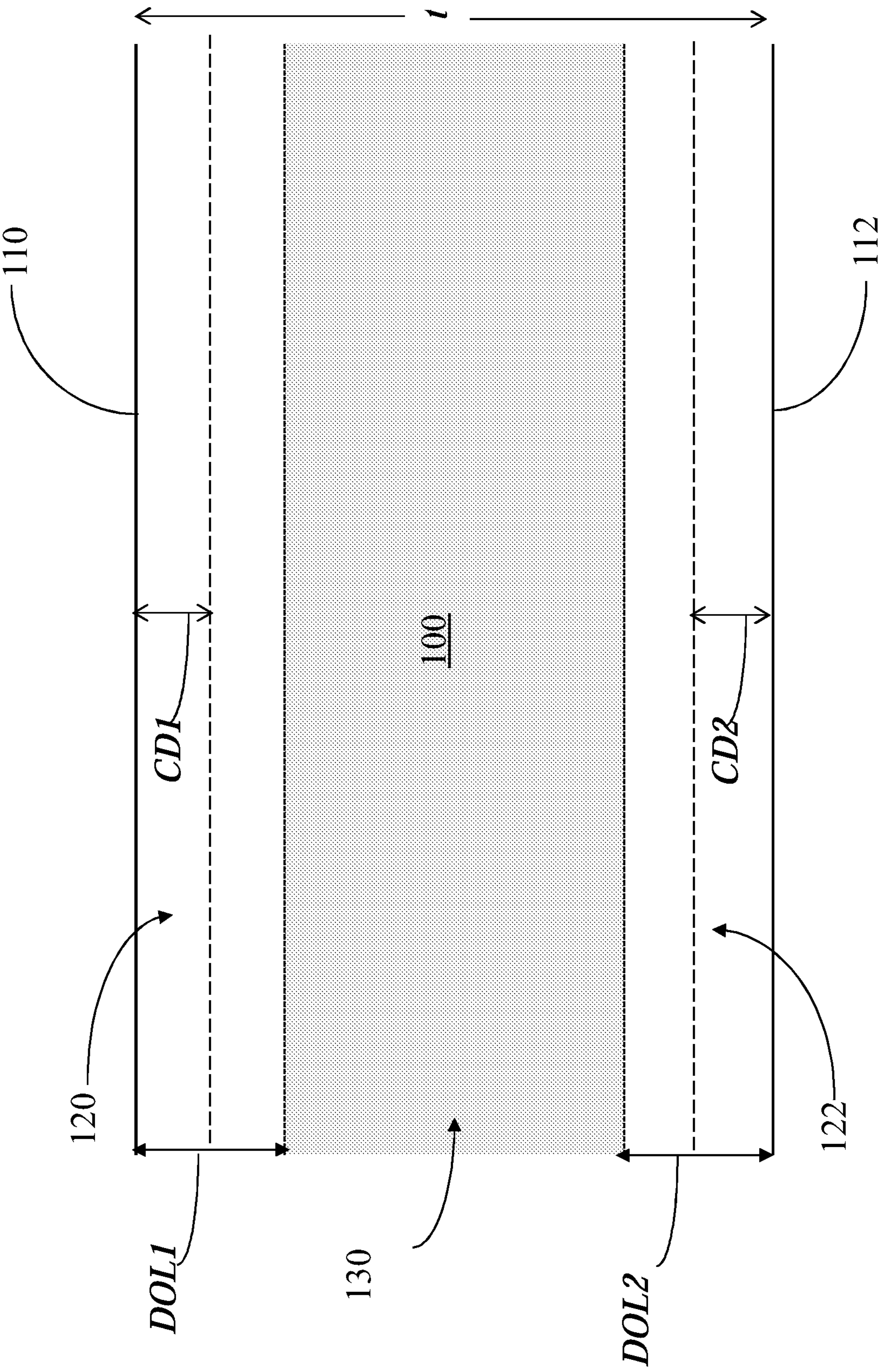

FIG. 1

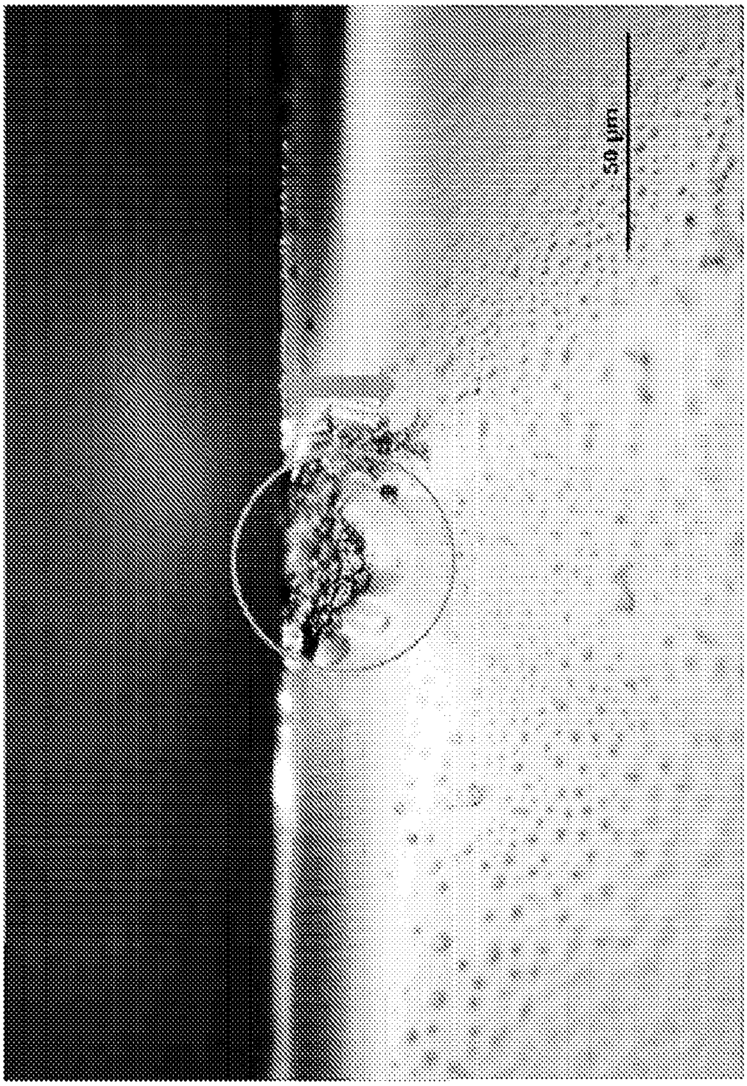

FIG. 2

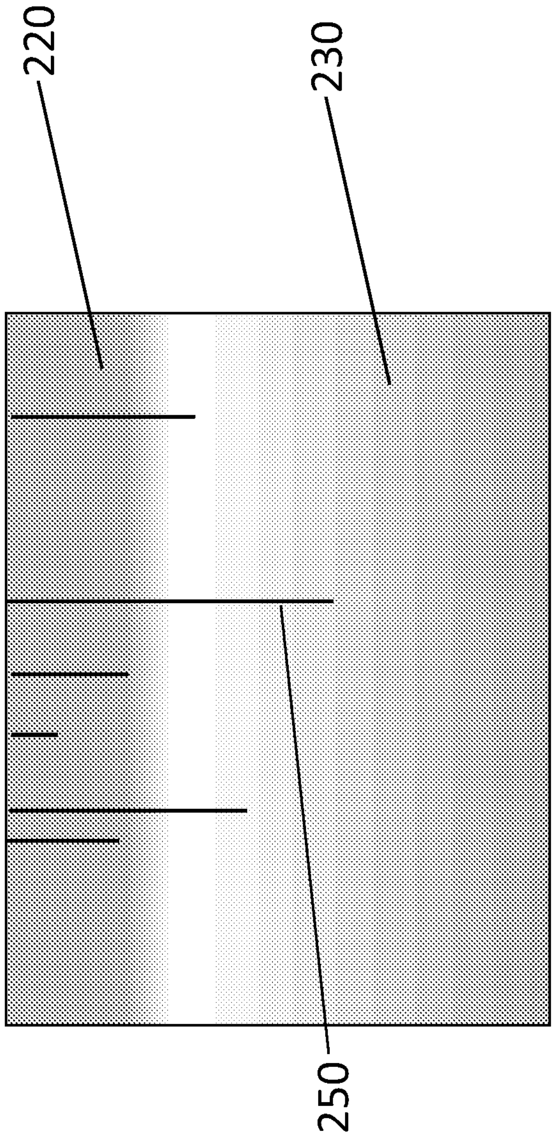

FIG. 3A

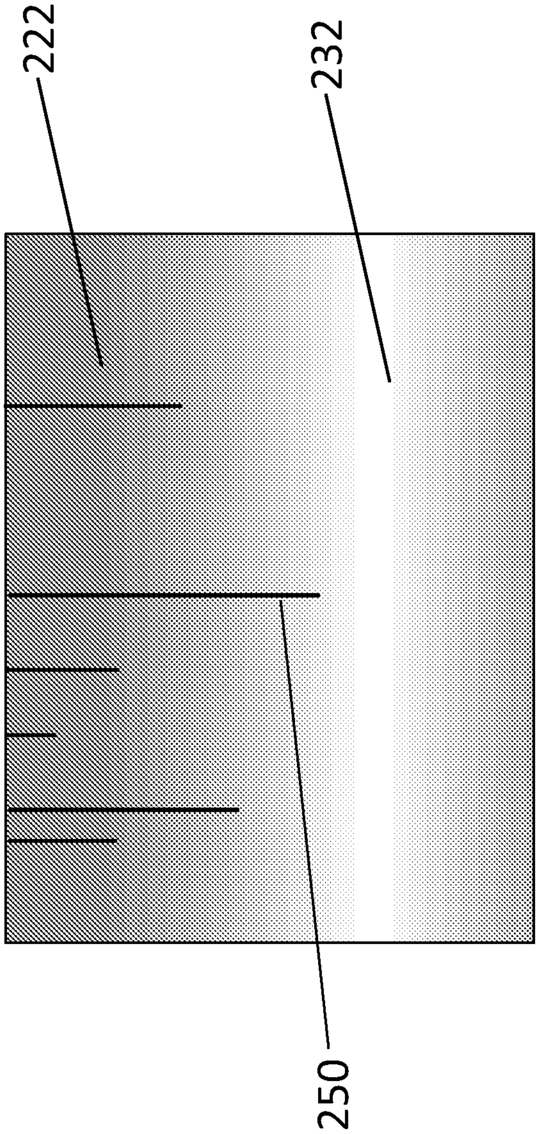

FIG. 3B

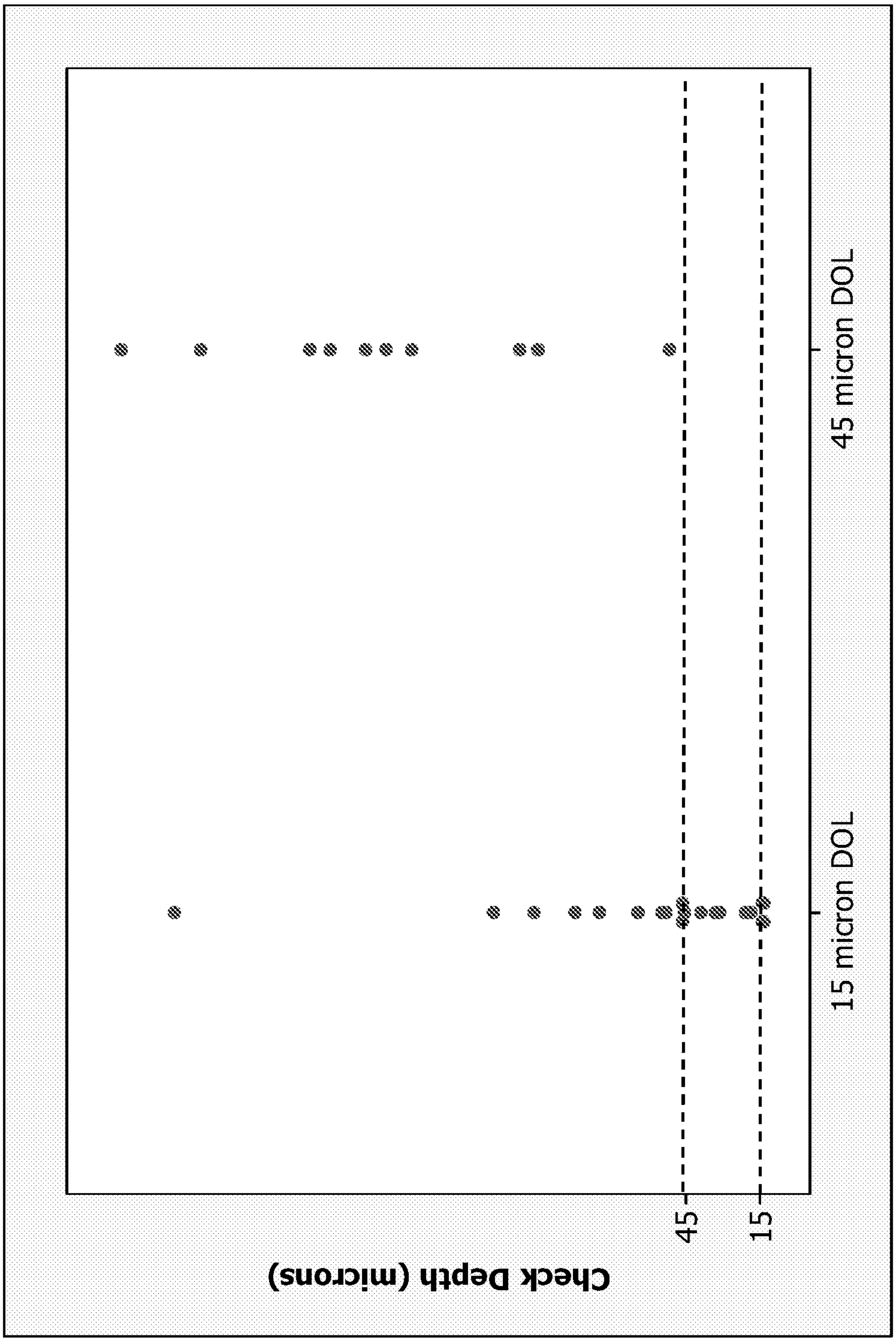

FIG. 4

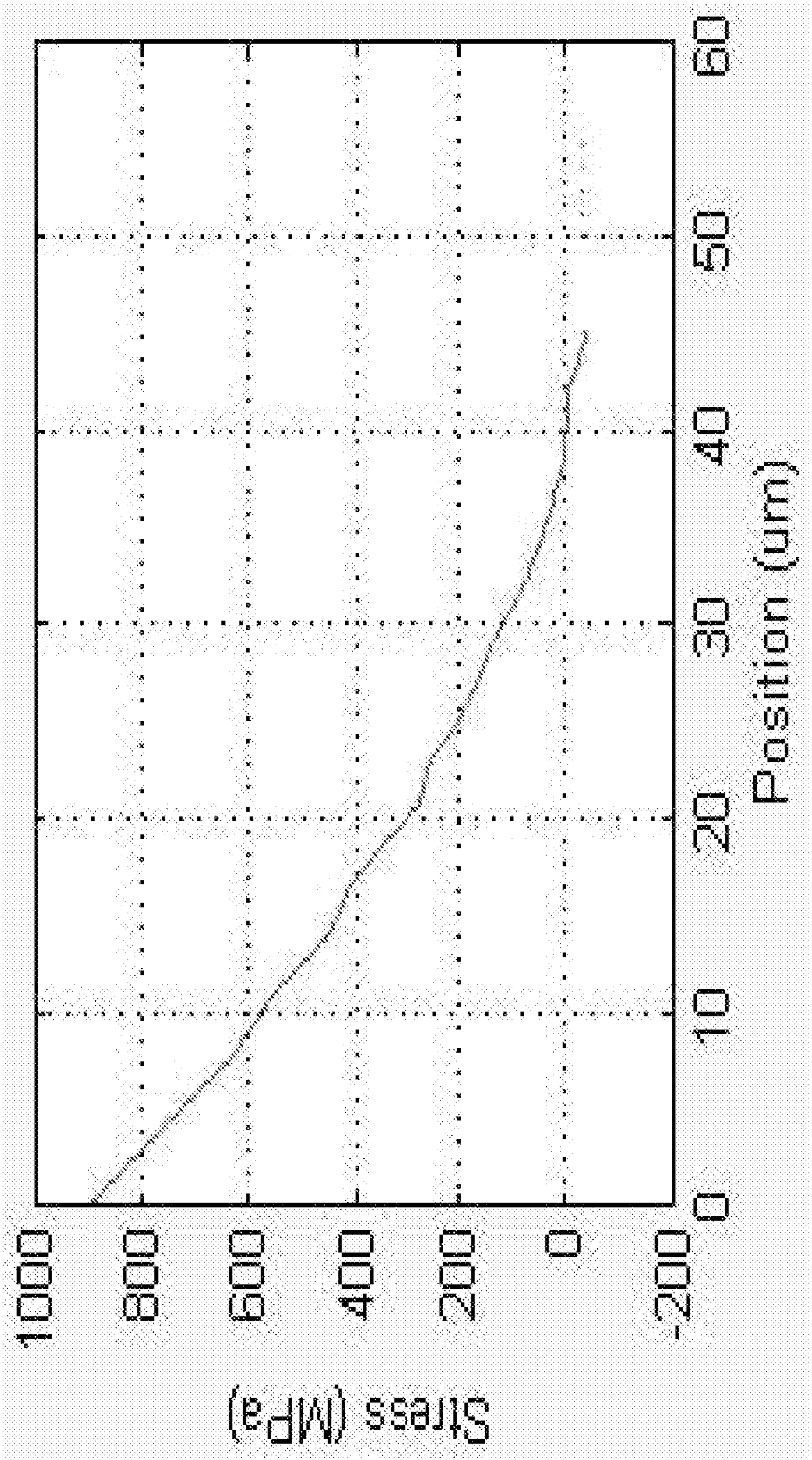
Stress (MPa)
1000
800
600
400
200
0
-200
0
10
20
30
40
50
60
Position (um)

FIG. 5

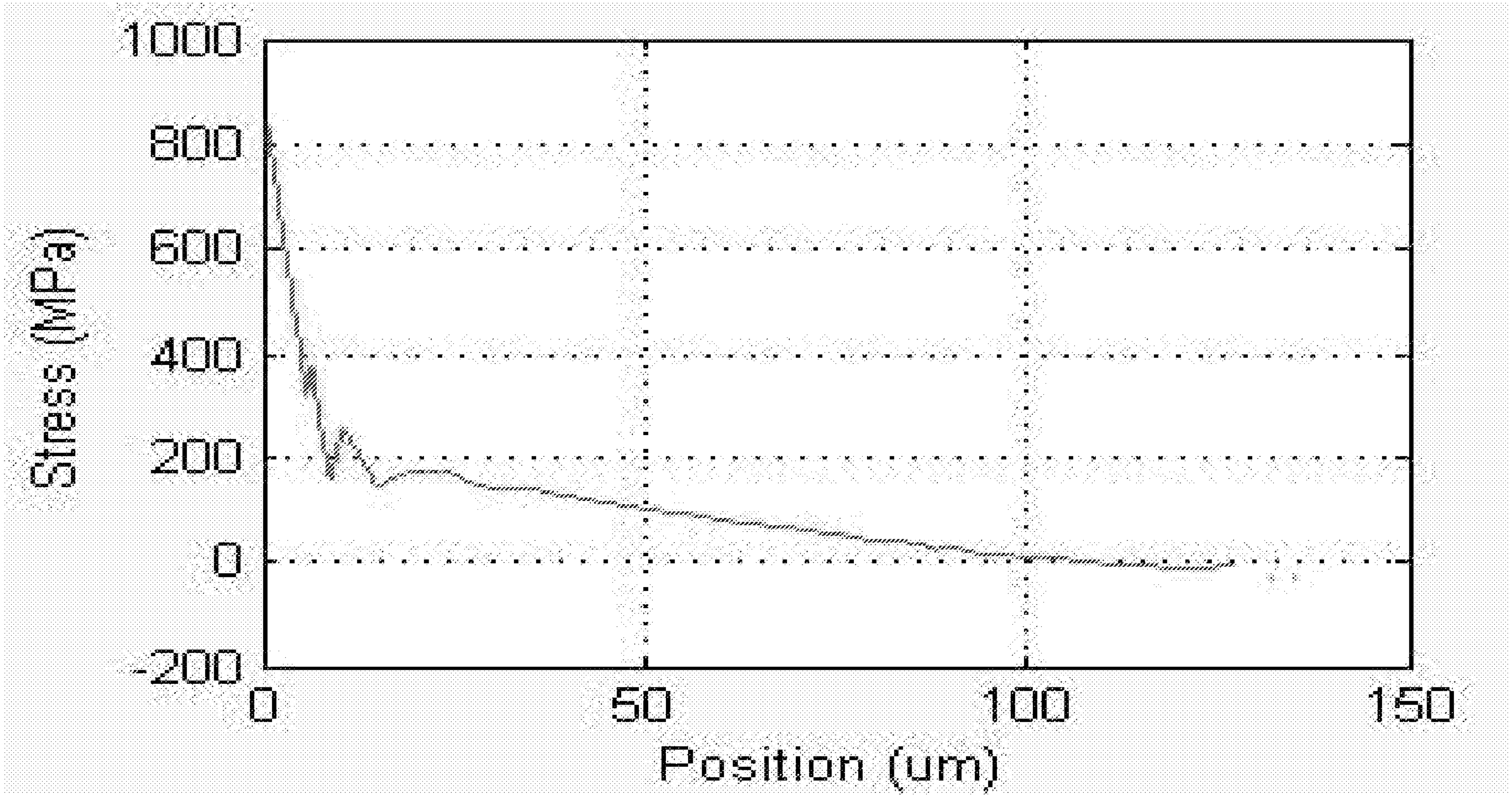

FIG. 6

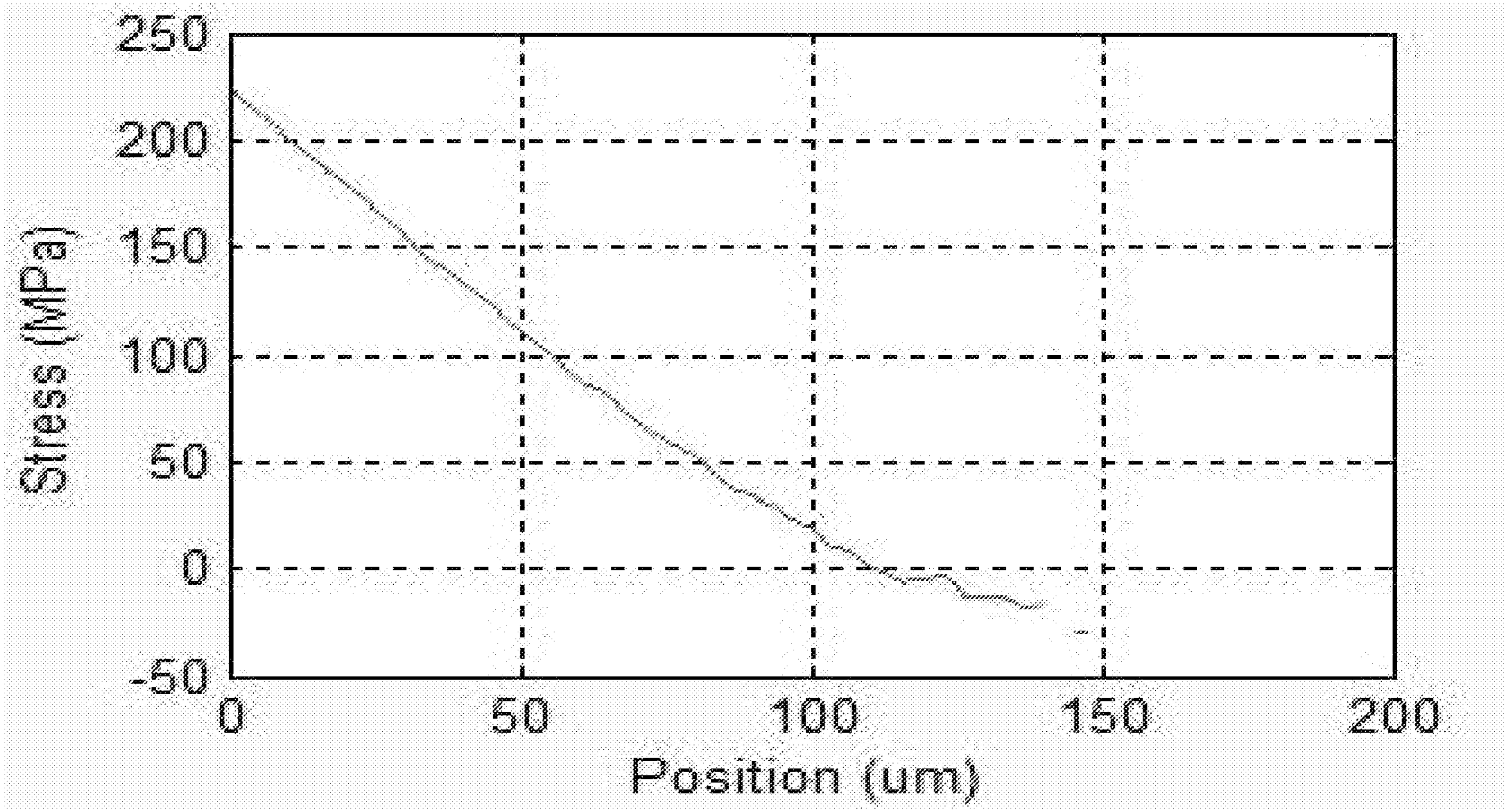

FIG. 7

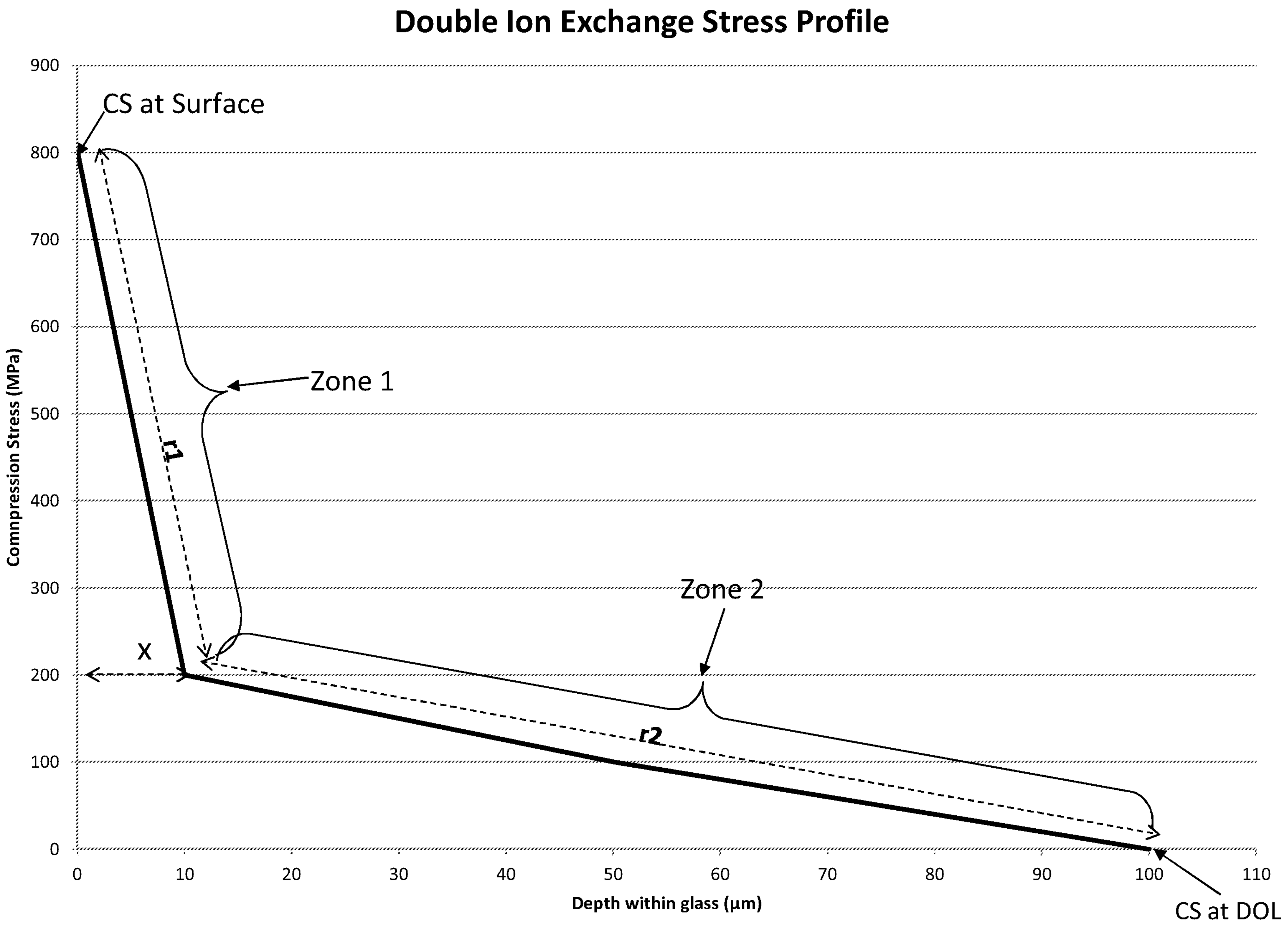
Double Ion Exchange Stress Profile
CS at Surface
Zone 1
r1
X
Zone 2
r2
CS at DOL
Comnpression Stress (MPa)
900
800
700
600
500
400
300
200
100
0
0
10
20
30
40
50
60
70
80
90
100
110
Depth within glass (µm)

FIG. 8

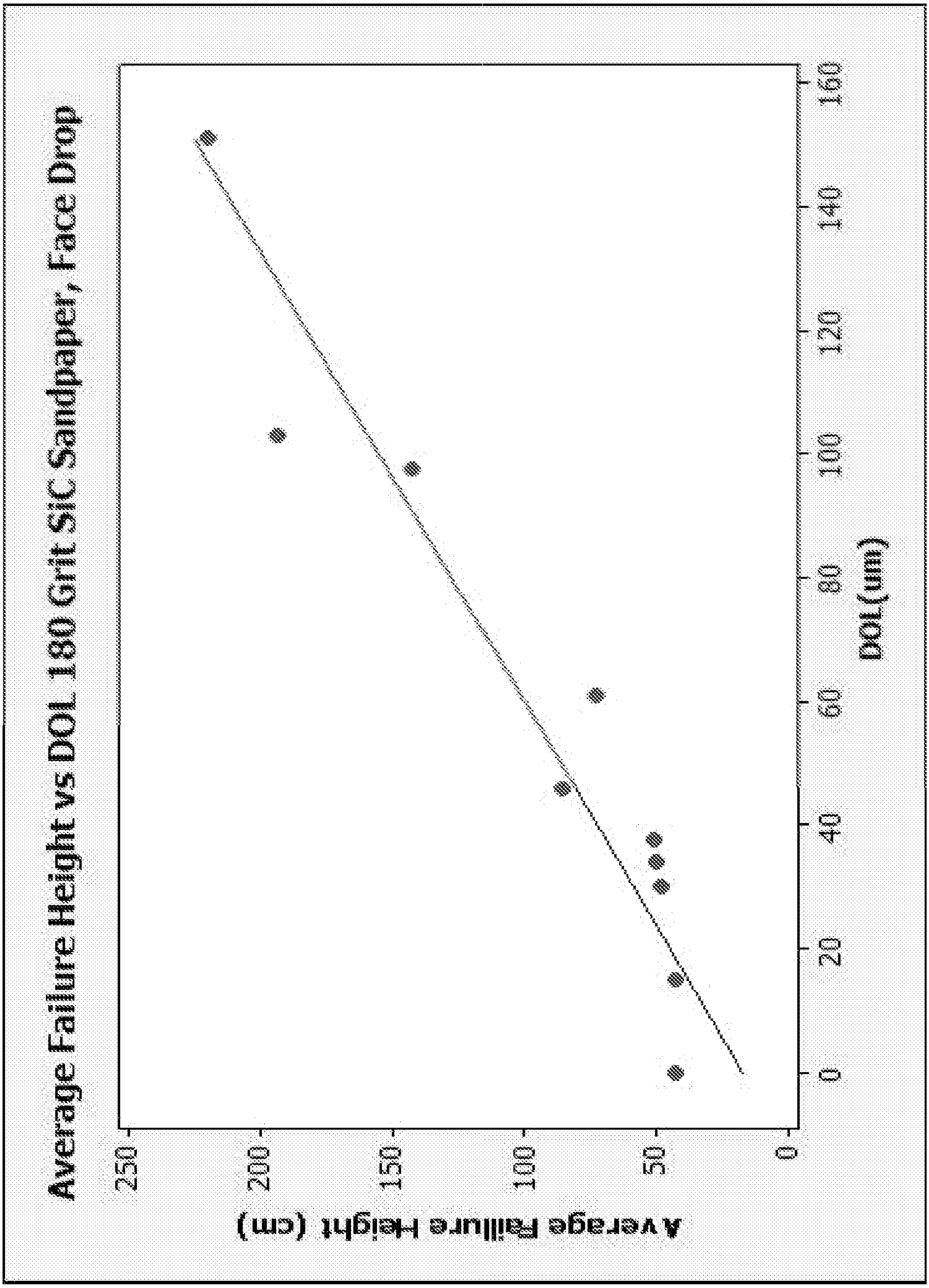
Average Failure Height vs DOL 180 Grit SiC Sandpaper, Face Drop
Average Failure Height (cm)
250
200
150
100
50
0
0
20
40
60
80
100
120
140
160
DOL (um)

FIG. 9

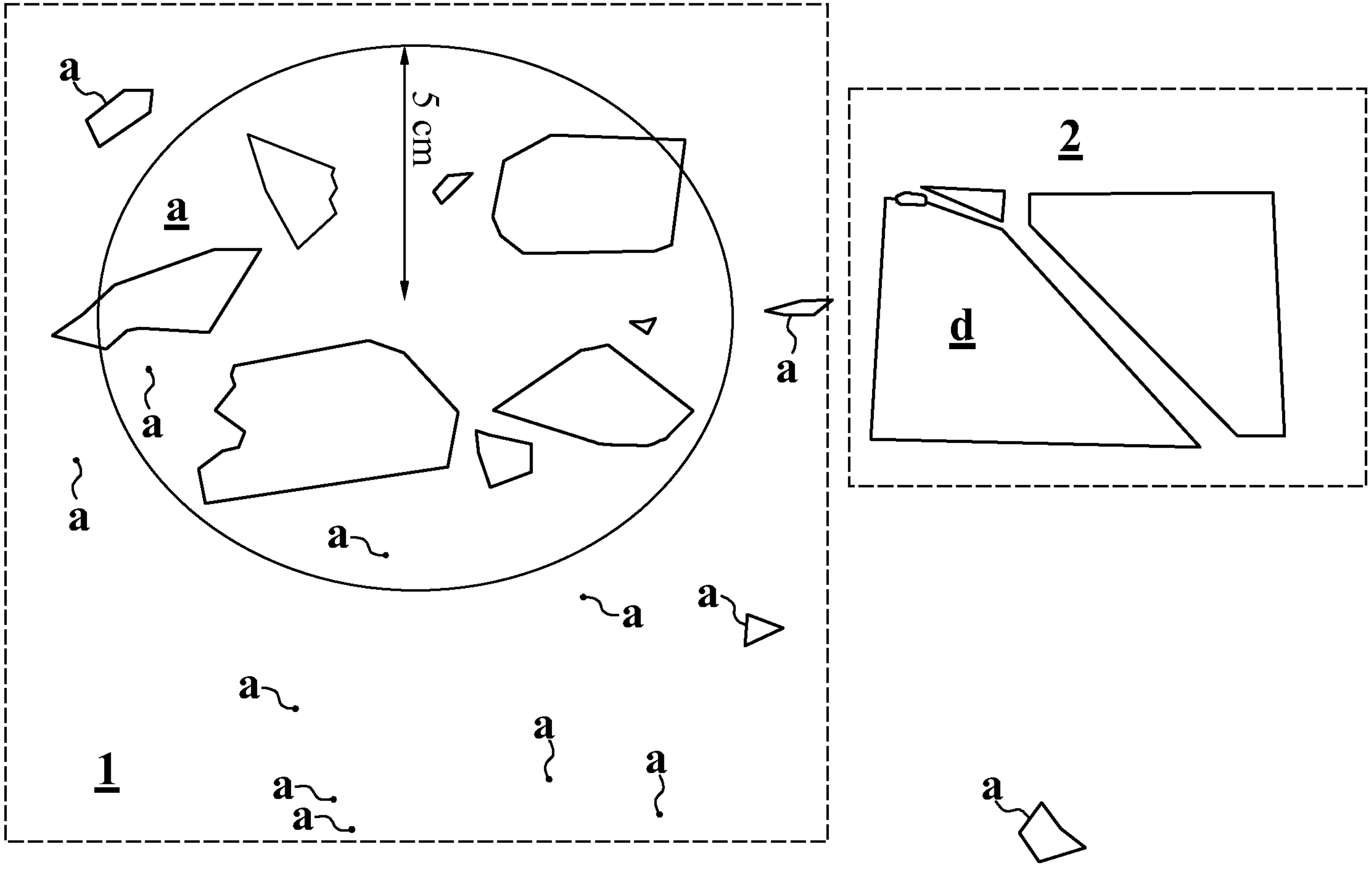

FIG. 10a

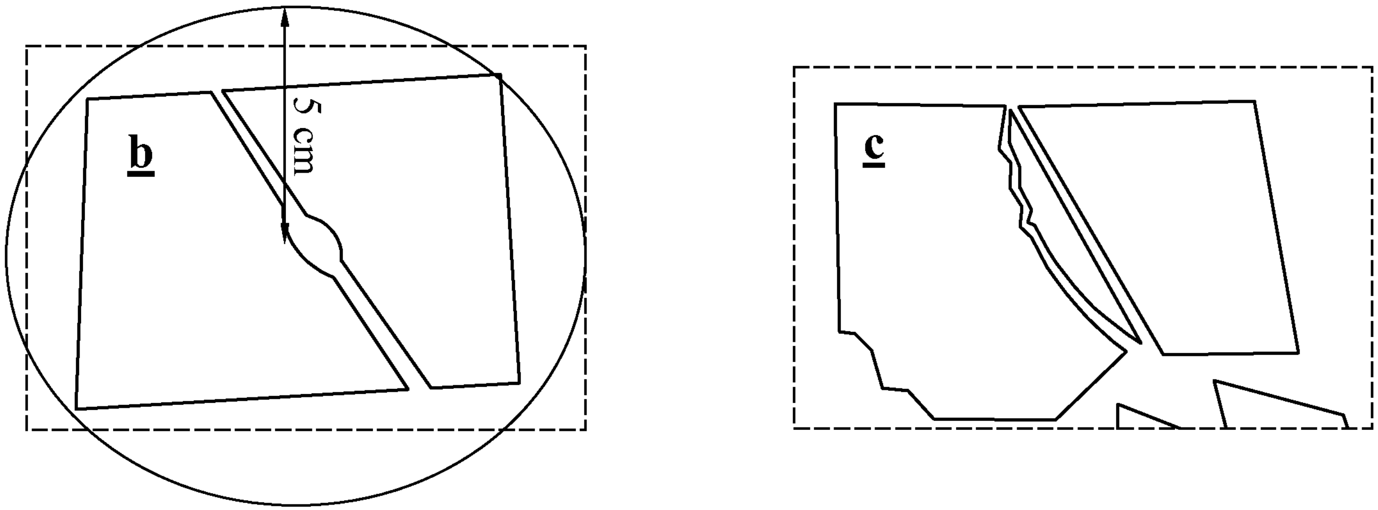

FIG. 10b