US 20040163967A1

(19) **United States**

(12) **Patent Application Publication** (10) **Pub. No.: US 2004/0163967 A1**

LaCamera et al. (43) **Pub. Date: Aug. 26, 2004**

(54) **INERT ANODE DESIGNS FOR REDUCED OPERATING VOLTAGE OF ALUMINUM PRODUCTION CELLS**

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(21) Appl. No.: **10/370,639**

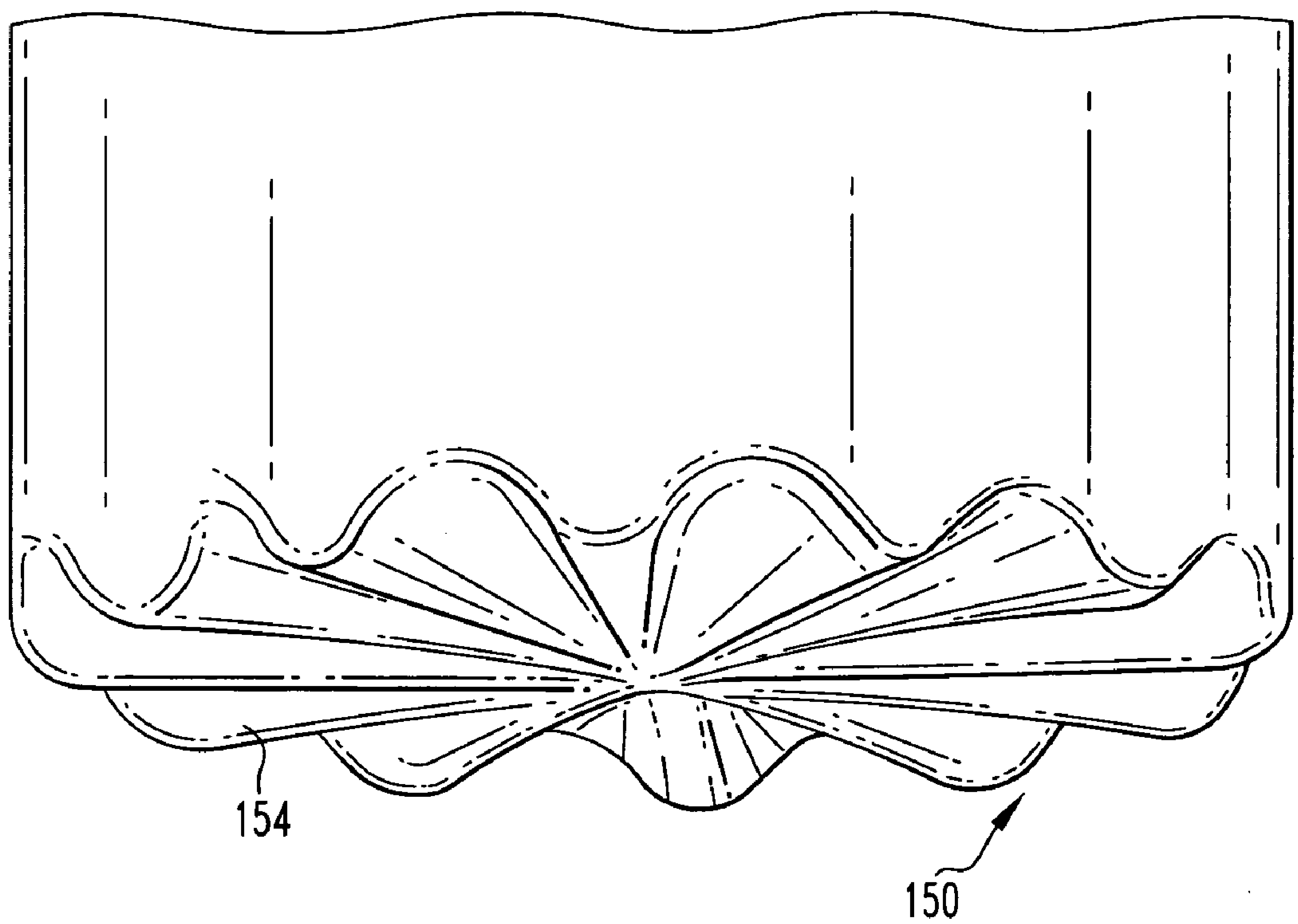
(22) Filed: **Feb. 20, 2003**

Publication Classification

(51) **Int. Cl.^{7}** **C25C 3/12**
(52) **U.S. Cl.** **205/381**

(57) **ABSTRACT**

Inert anodes useful in electrolytic aluminum production cells are disclosed. The inert anodes have sloped bottom surfaces with controlled bubble release angles. In one embodiment, the bottom surface is substantially conical with a bubble release angle of up to 30 degrees. The cross-sectional size of the inert anodes is also controlled in order to maximize efficiency of the cells. The inert anodes may be provided in arrays in aluminum production cells in order to achieve commercial cell currents.



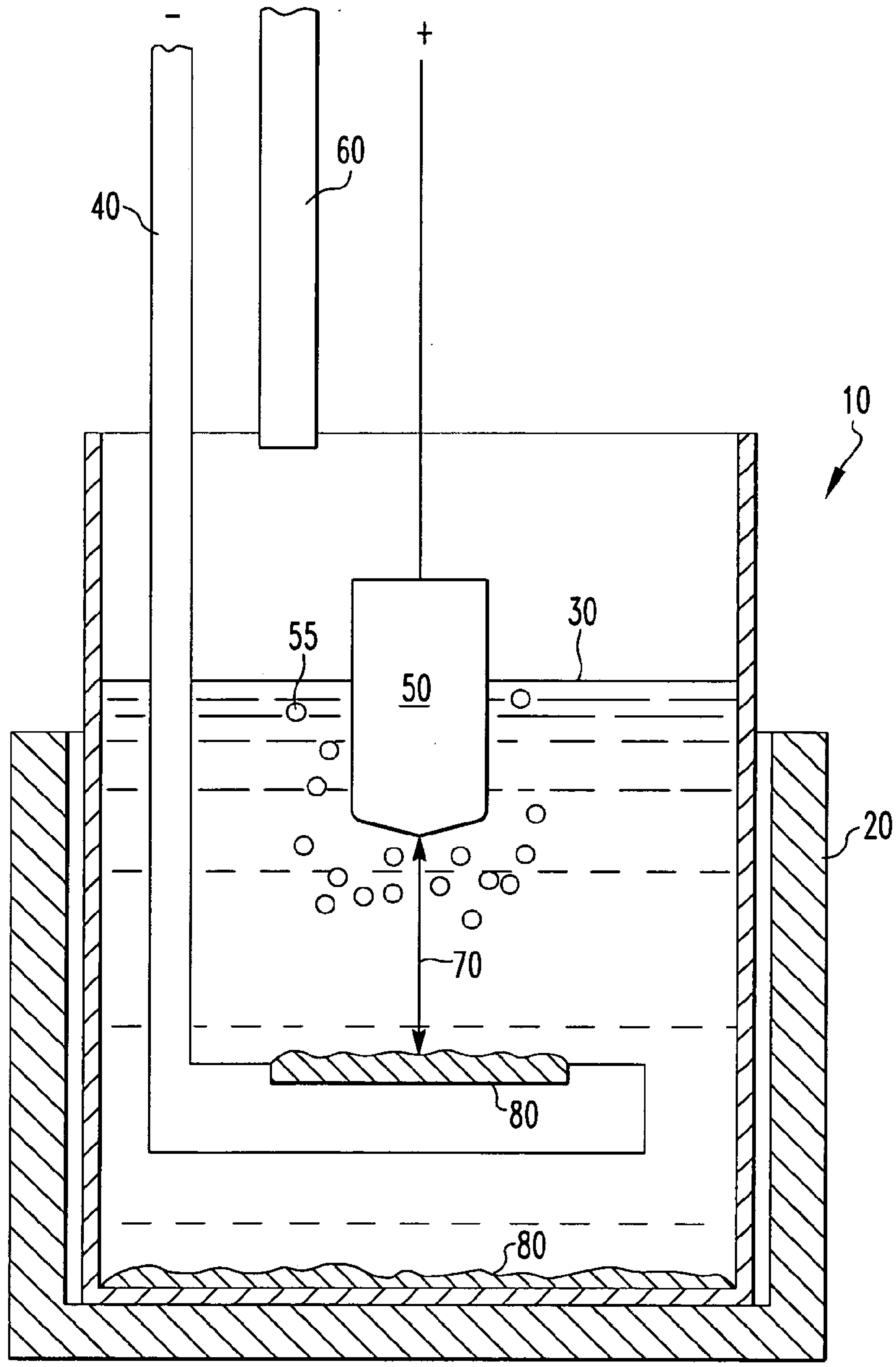


FIG.1

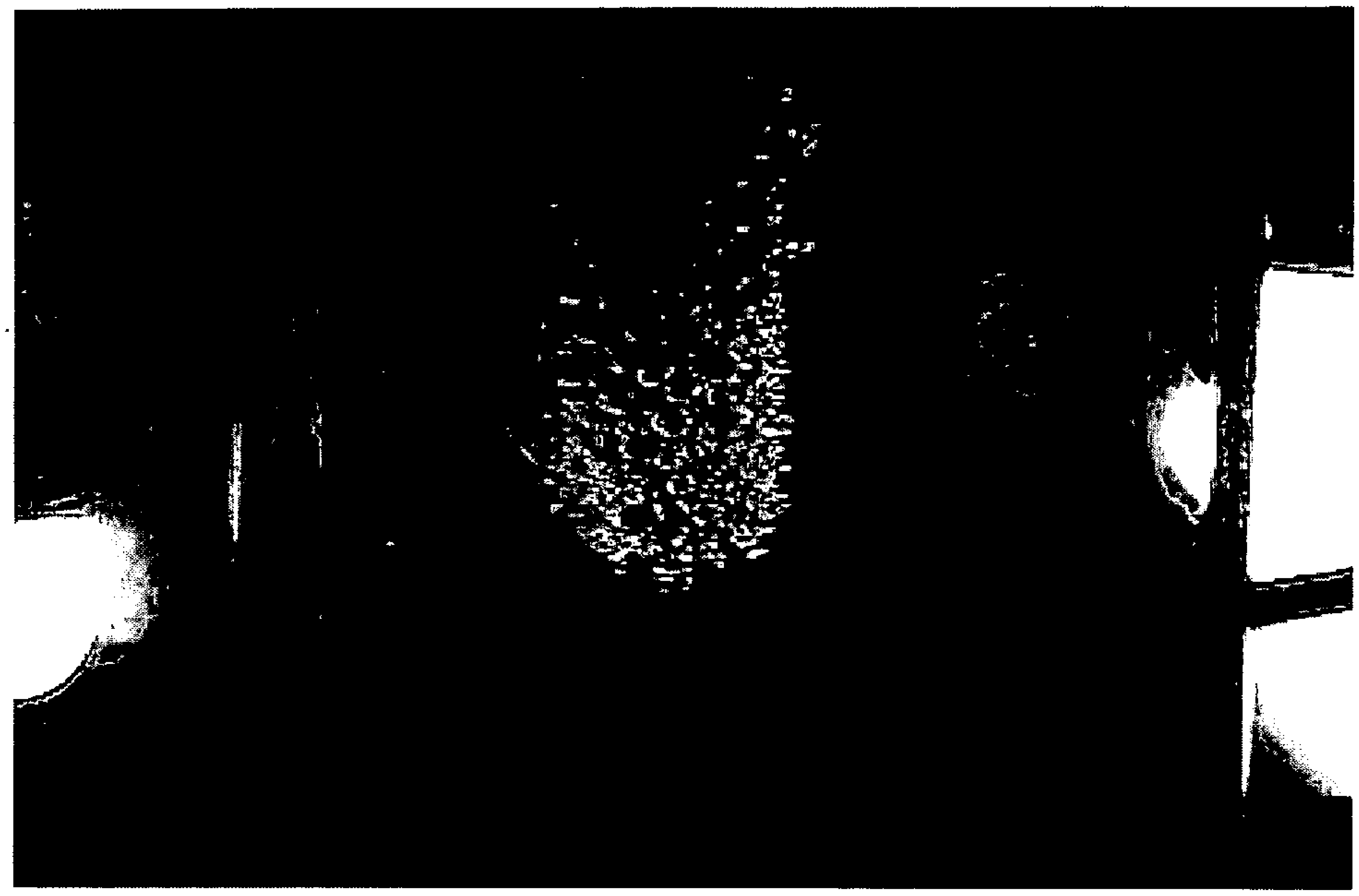
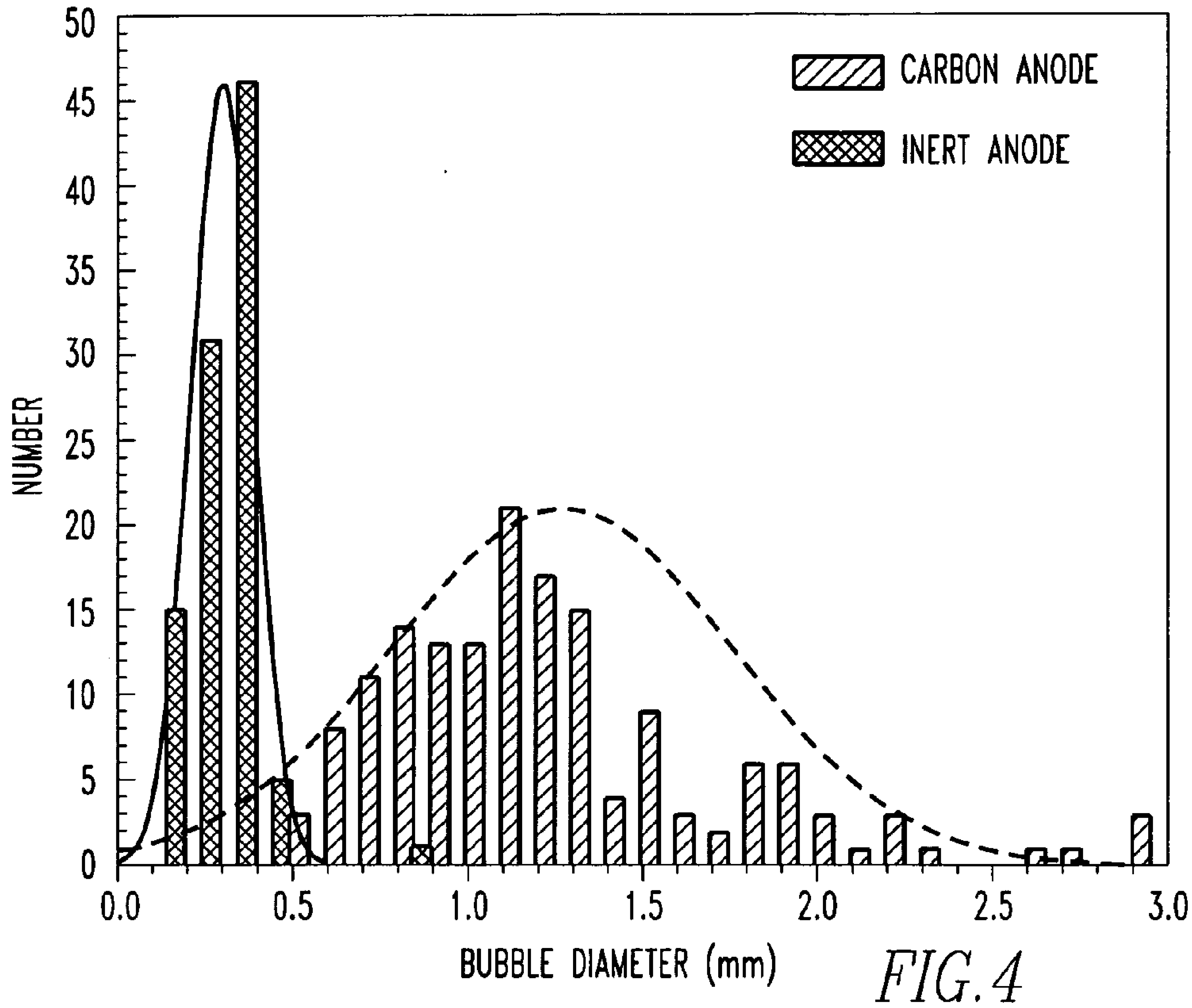


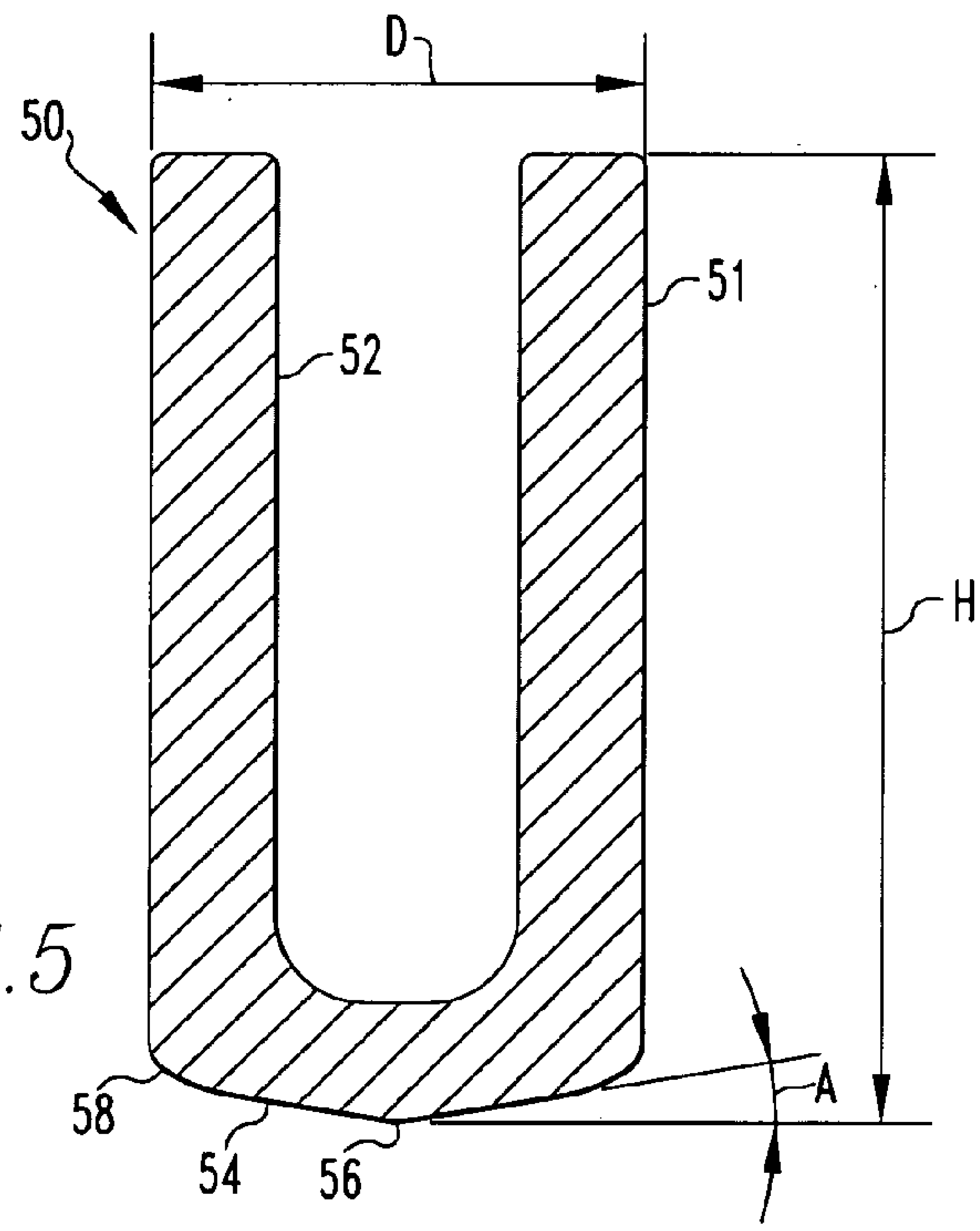
FIG. 2

FIG. 3



CARBON ANODE
INERT ANODE
NUMBER
BUBBLE DIAMETER (mm)

FIG. 4



D
50
51
52
H
A
58
54
56

FIG. 5

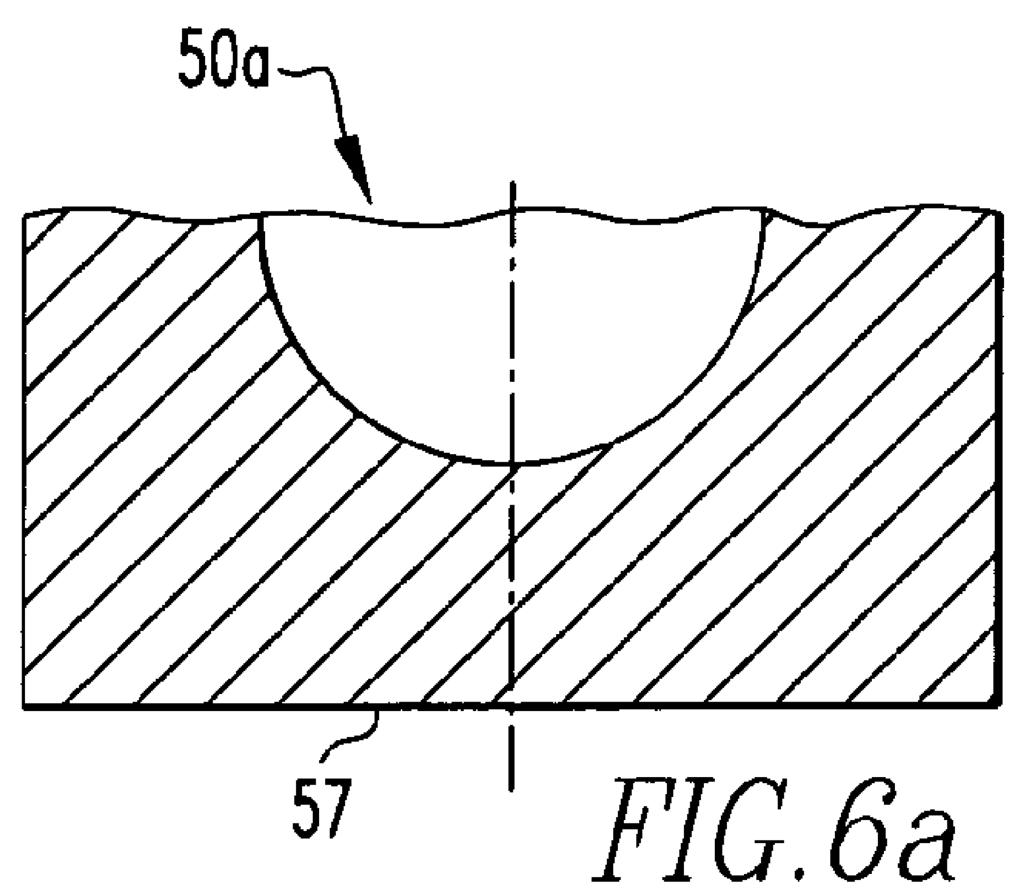


FIG.6a

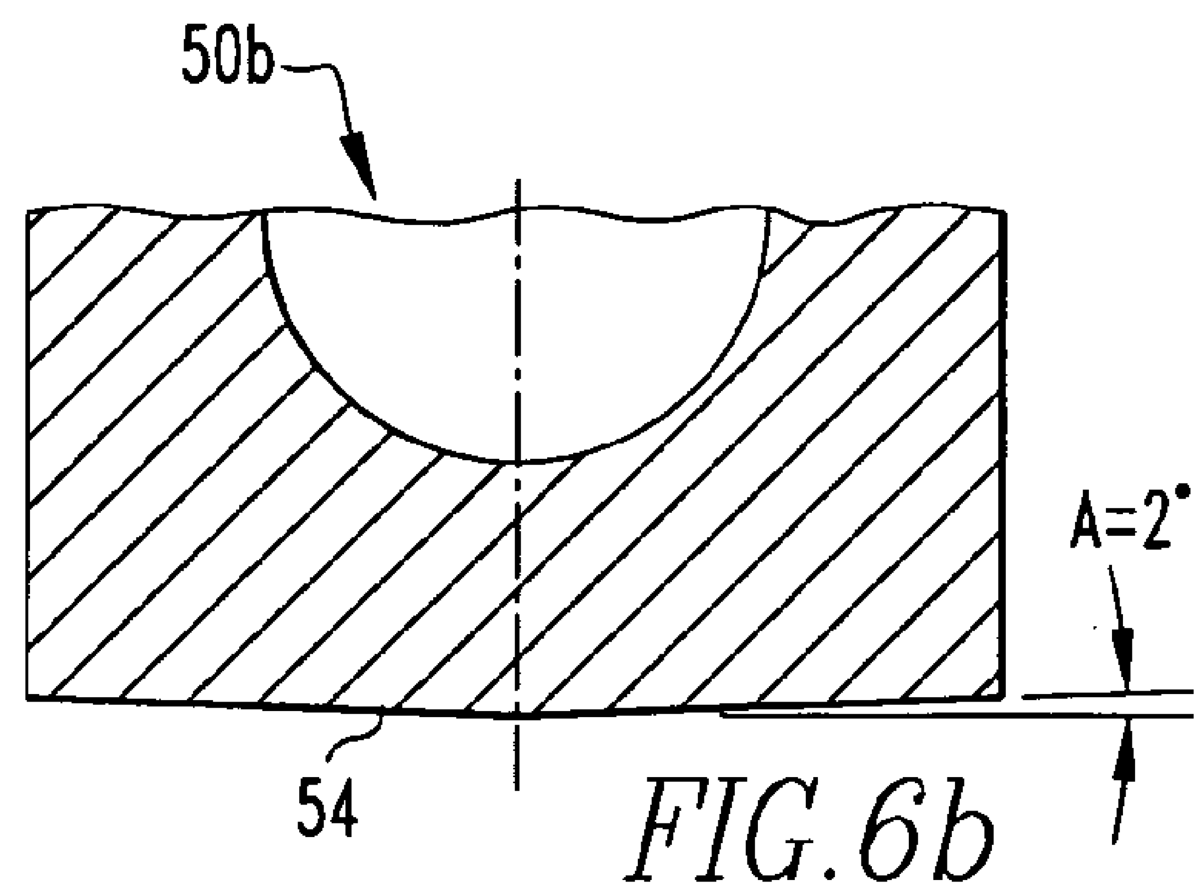


FIG.6b

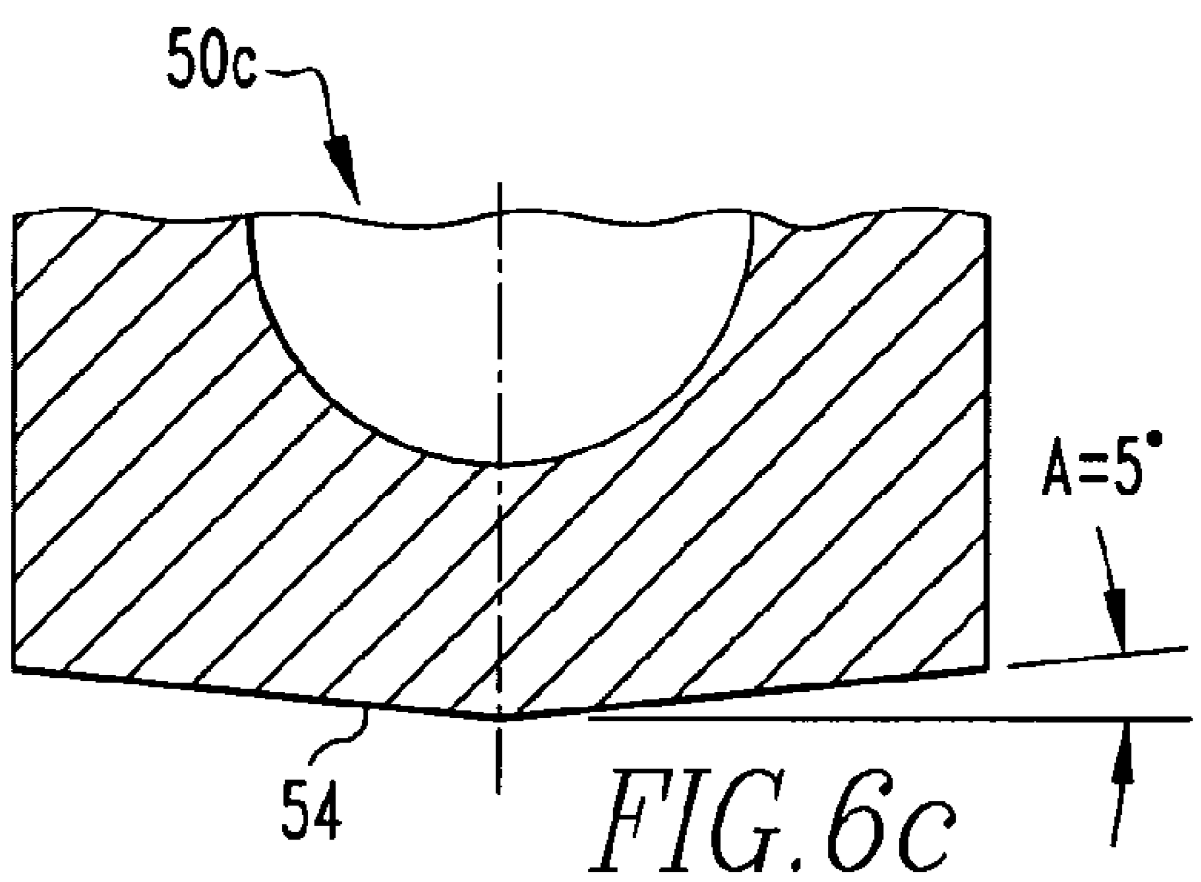


FIG.6c

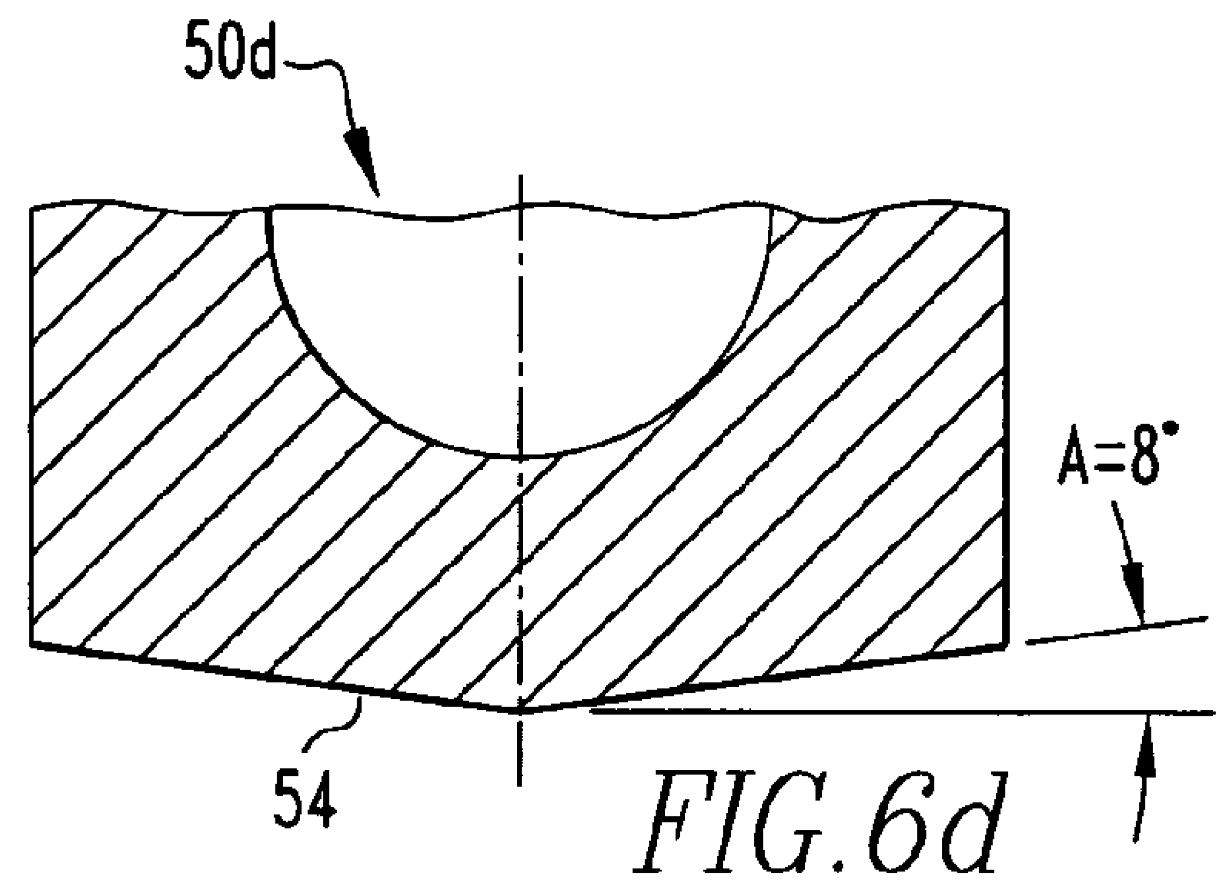


FIG.6d

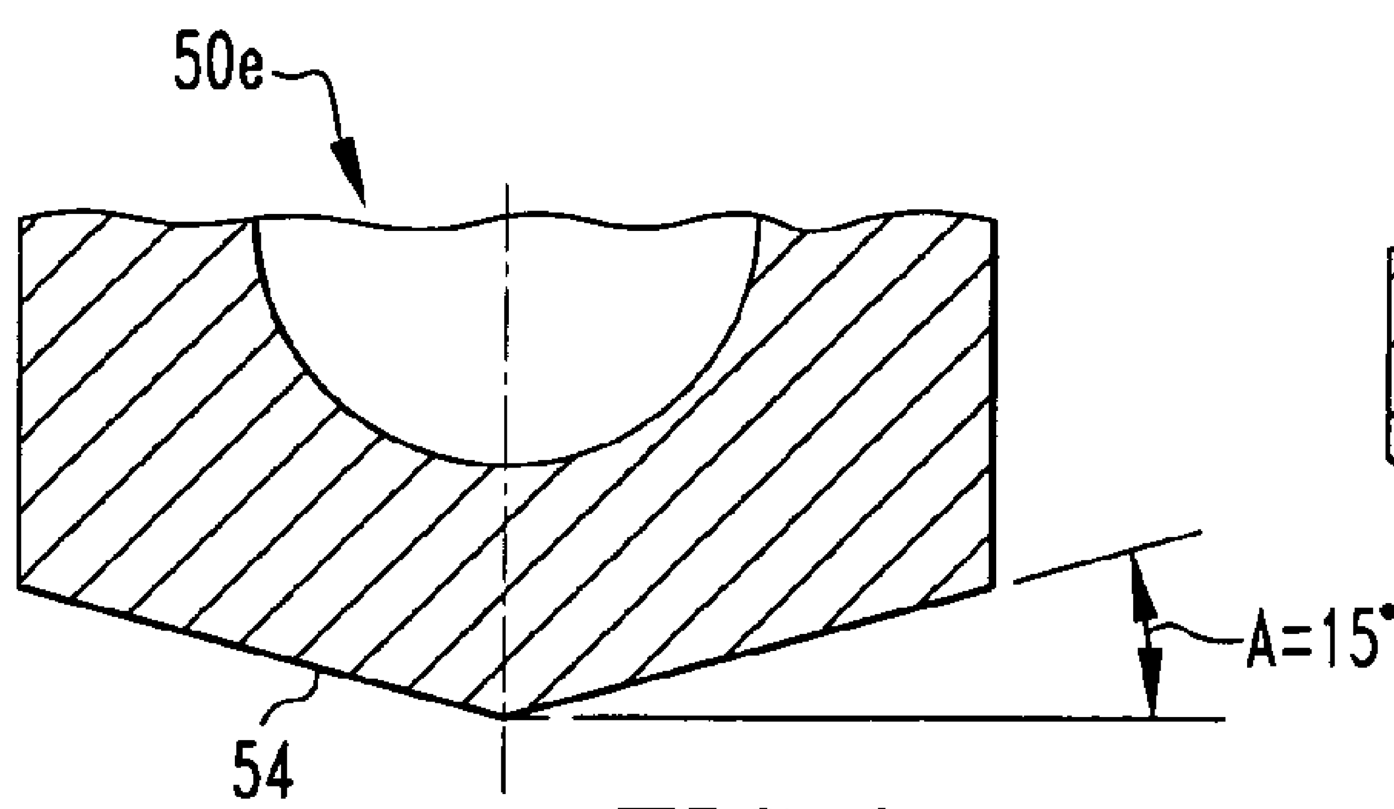


FIG.6e

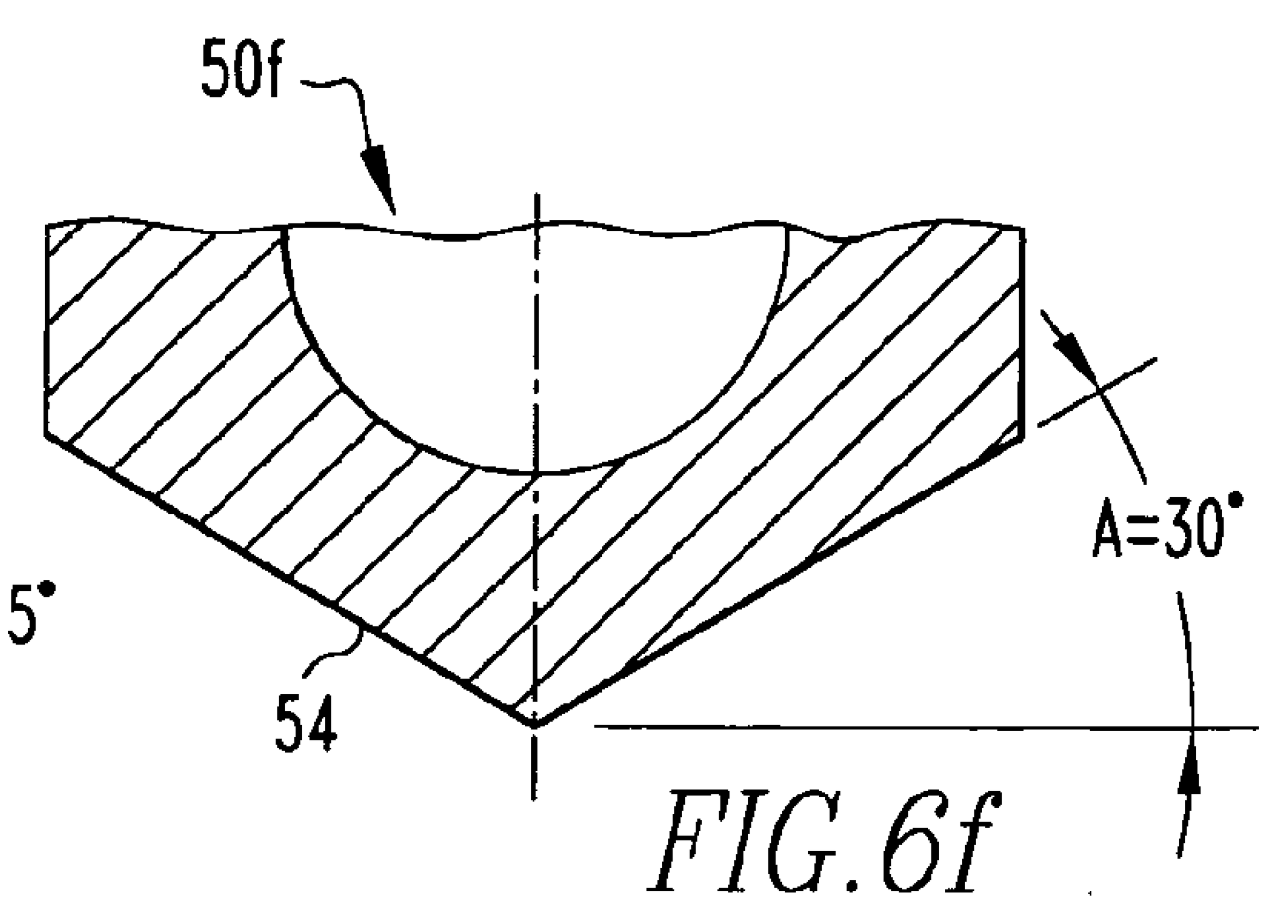


FIG.6f

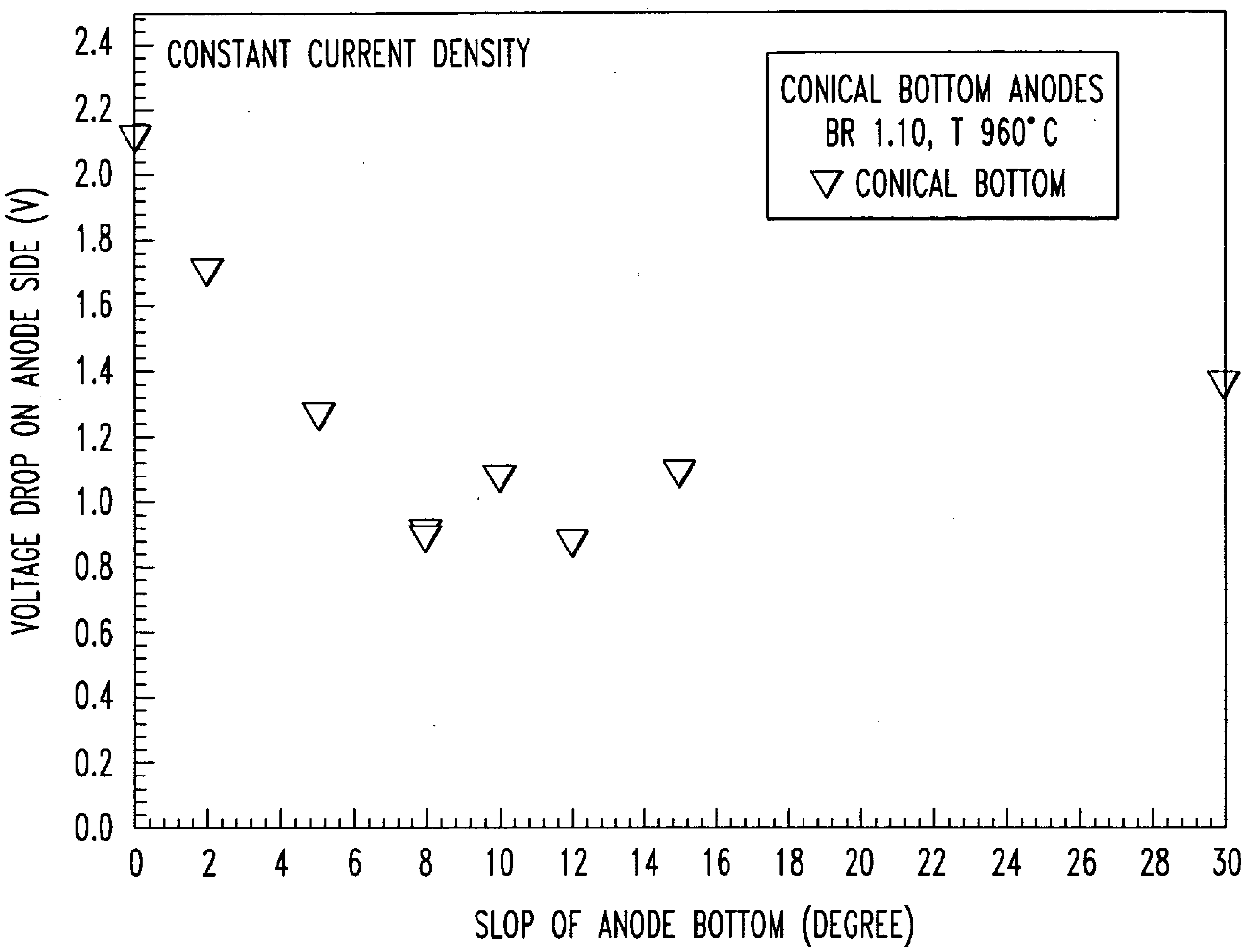

CONSTANT CURRENT DENSITY
CONICAL BOTTOM ANODES
BR 1.10, T 960°C
CONICAL BOTTOM
VOLTAGE DROP ON ANODE SIDE (V)
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
SLOP OF ANODE BOTTOM (DEGREE)

FIG. 7

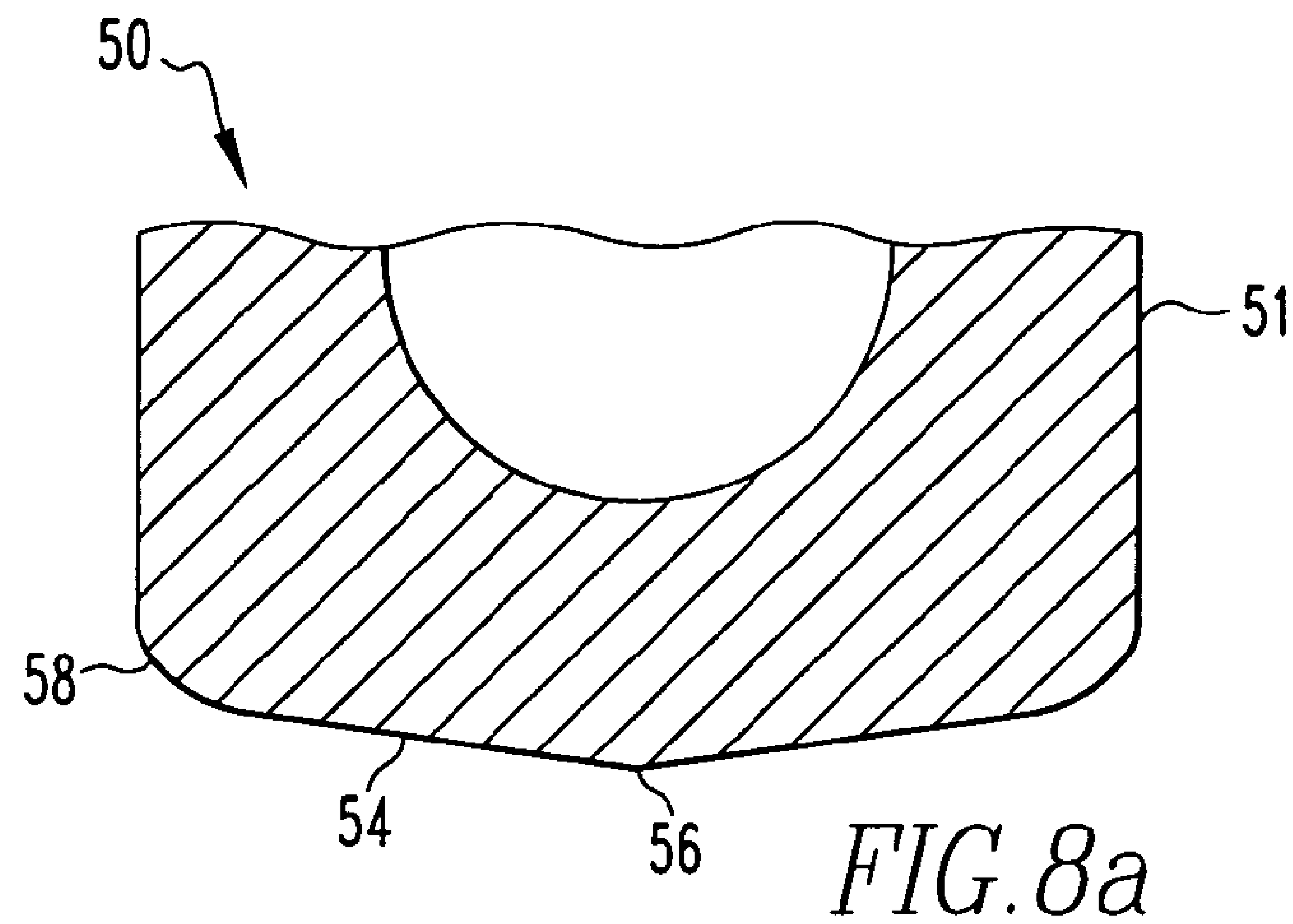


FIG. 8a

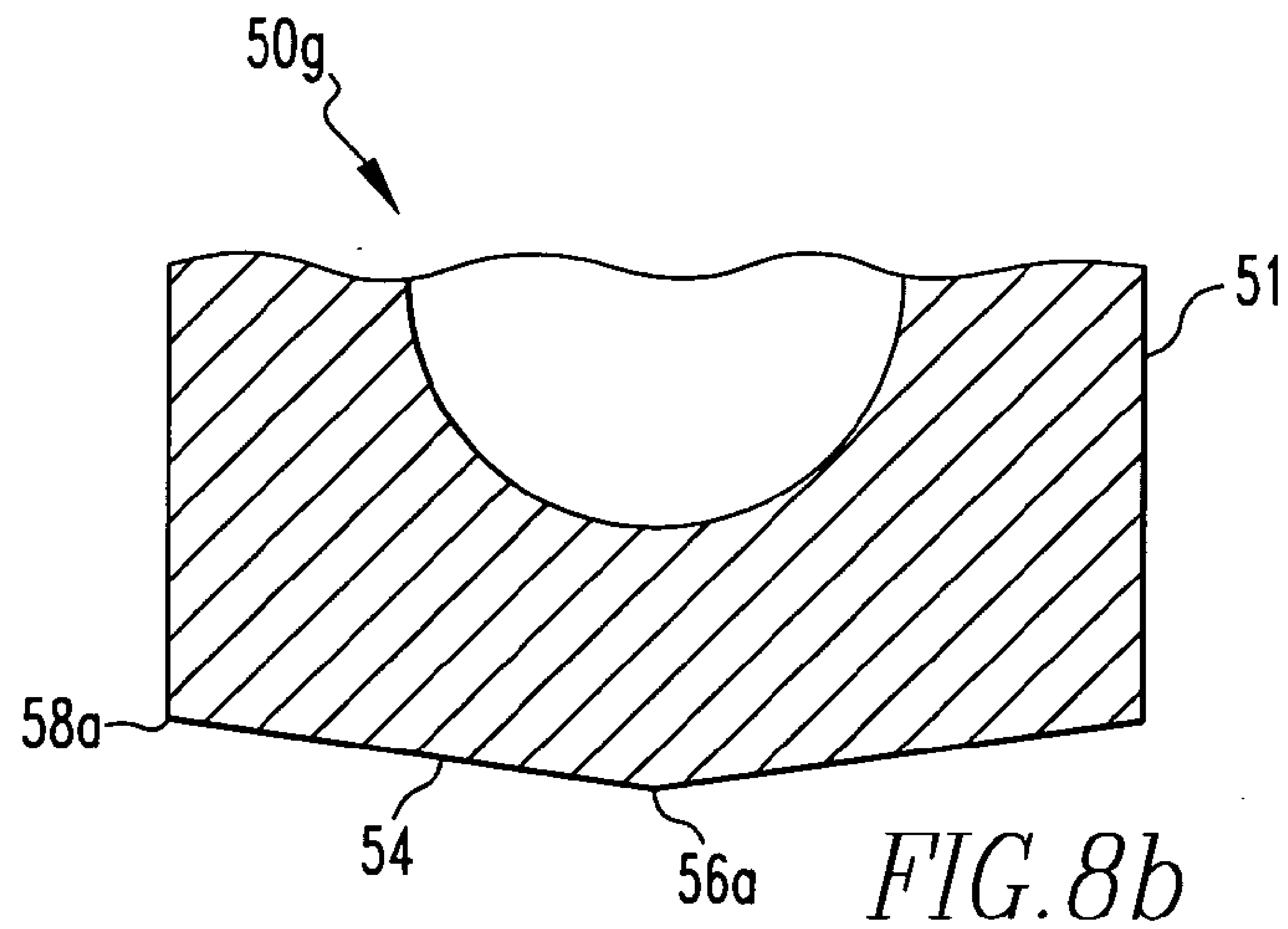


FIG. 8b

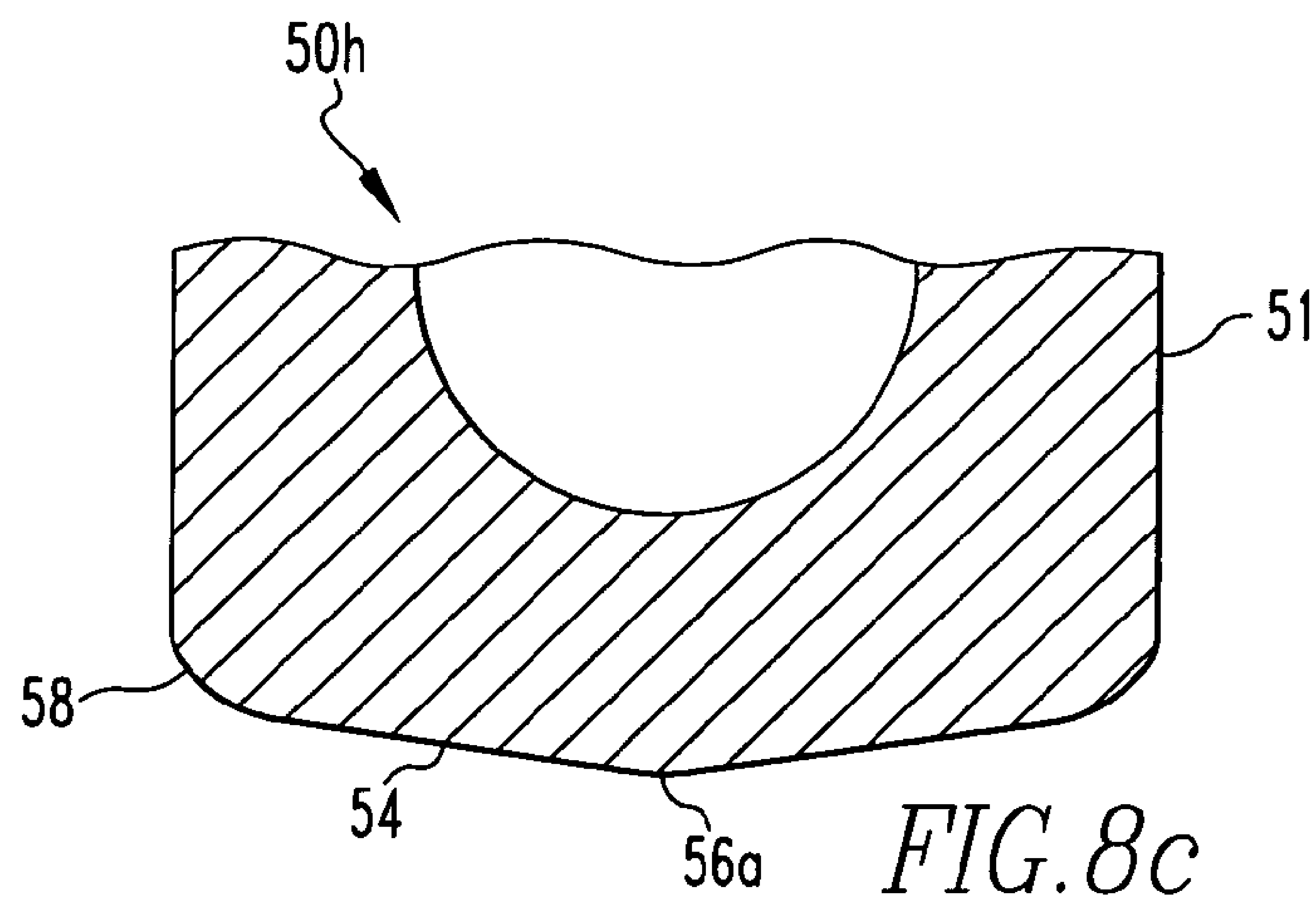


FIG. 8c

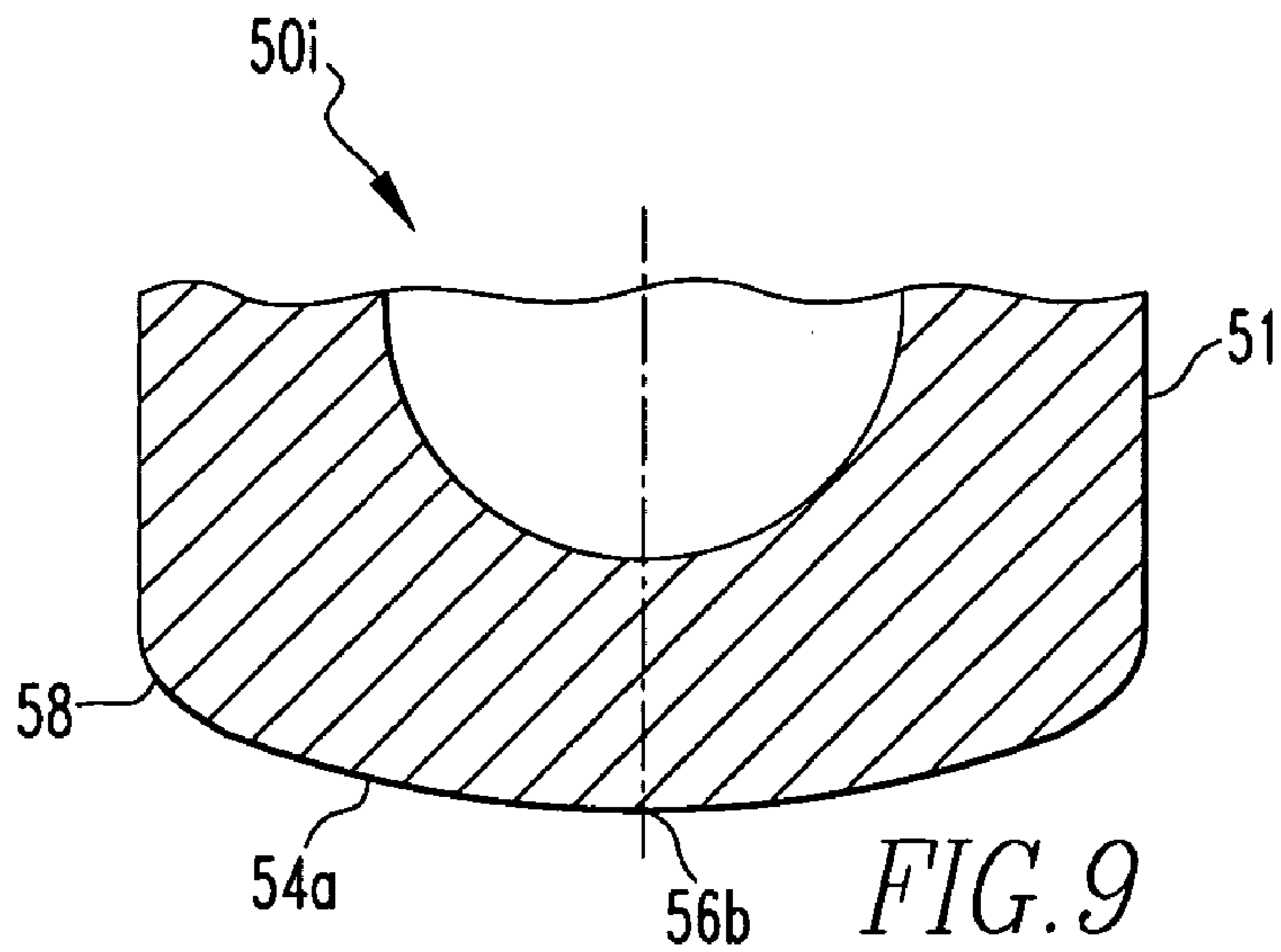


FIG. 9

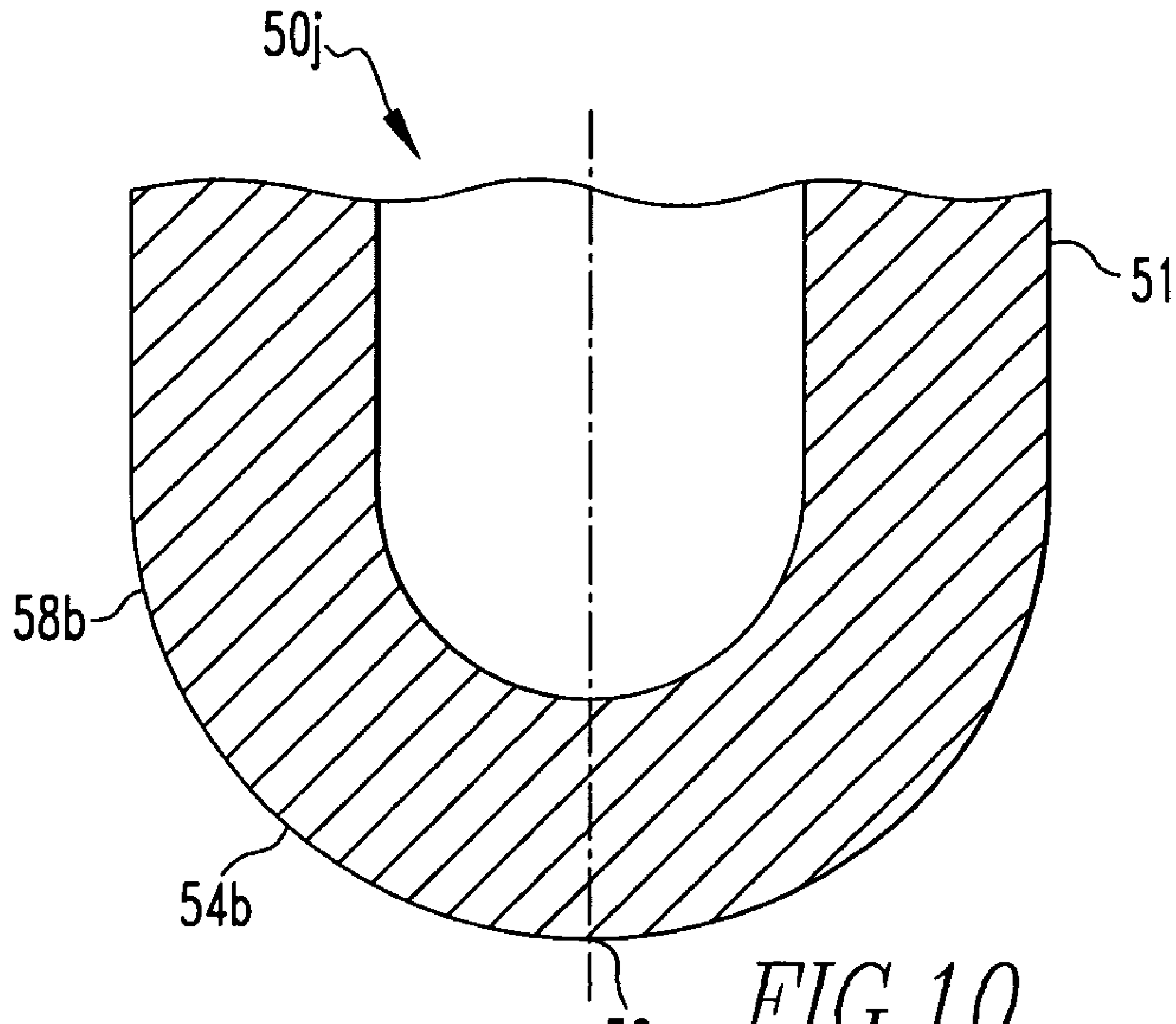


FIG. 10

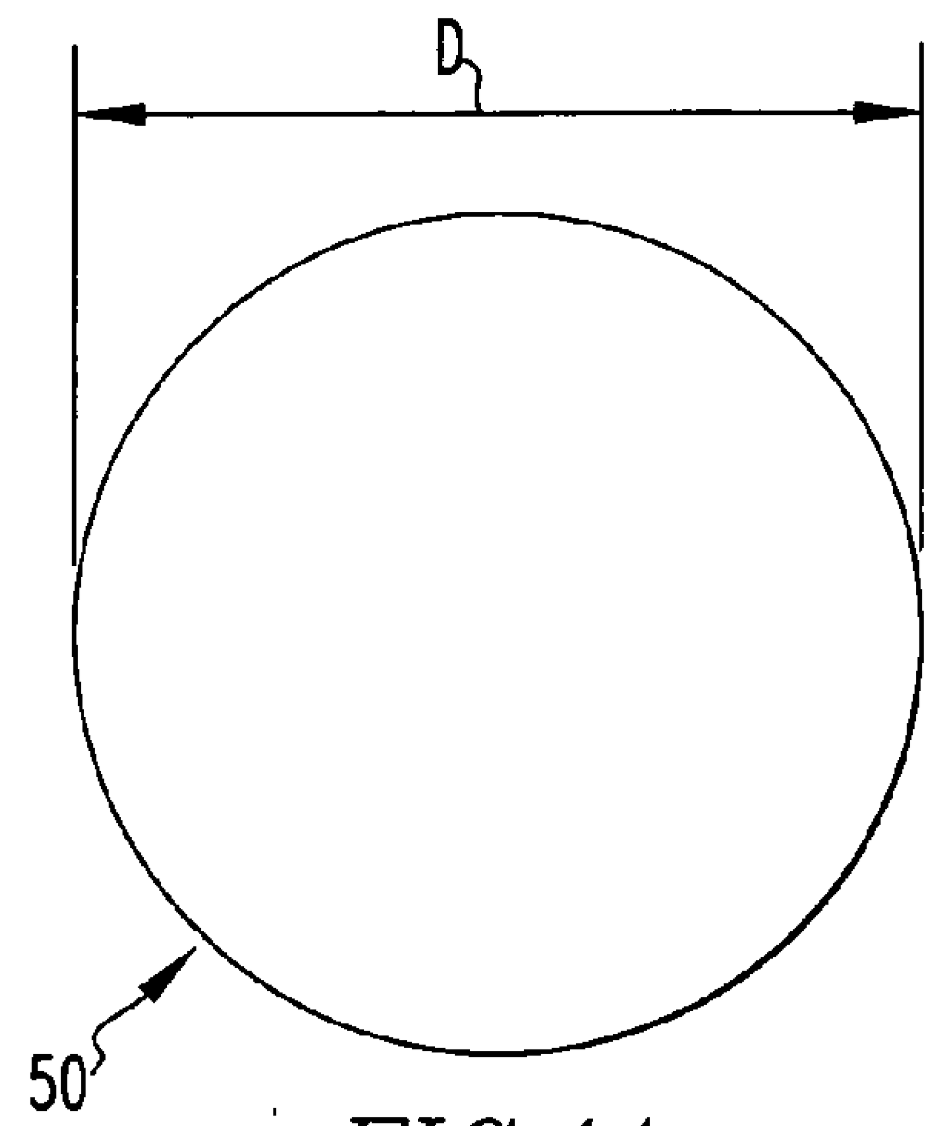


FIG.11

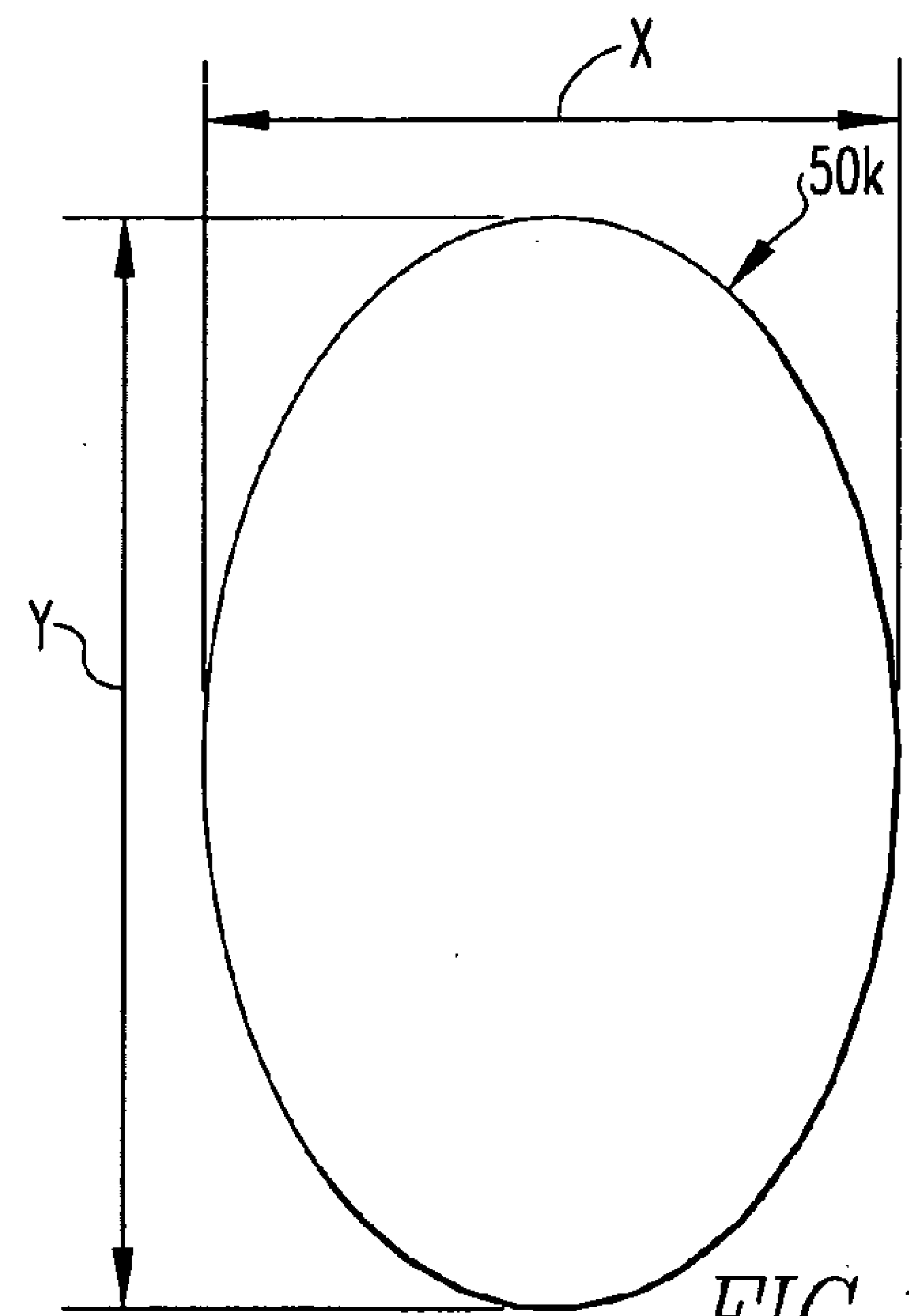


FIG.12

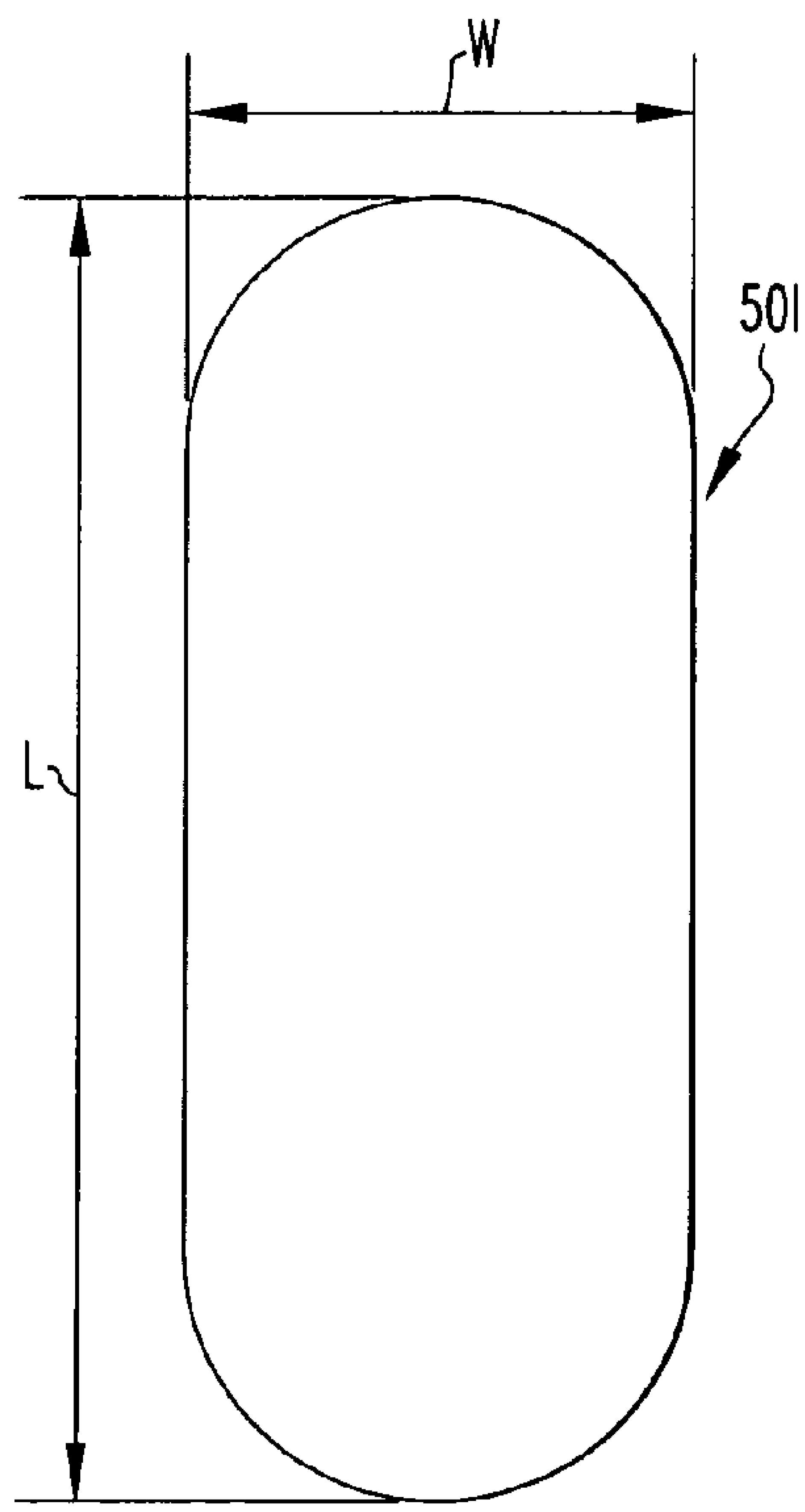


FIG.13

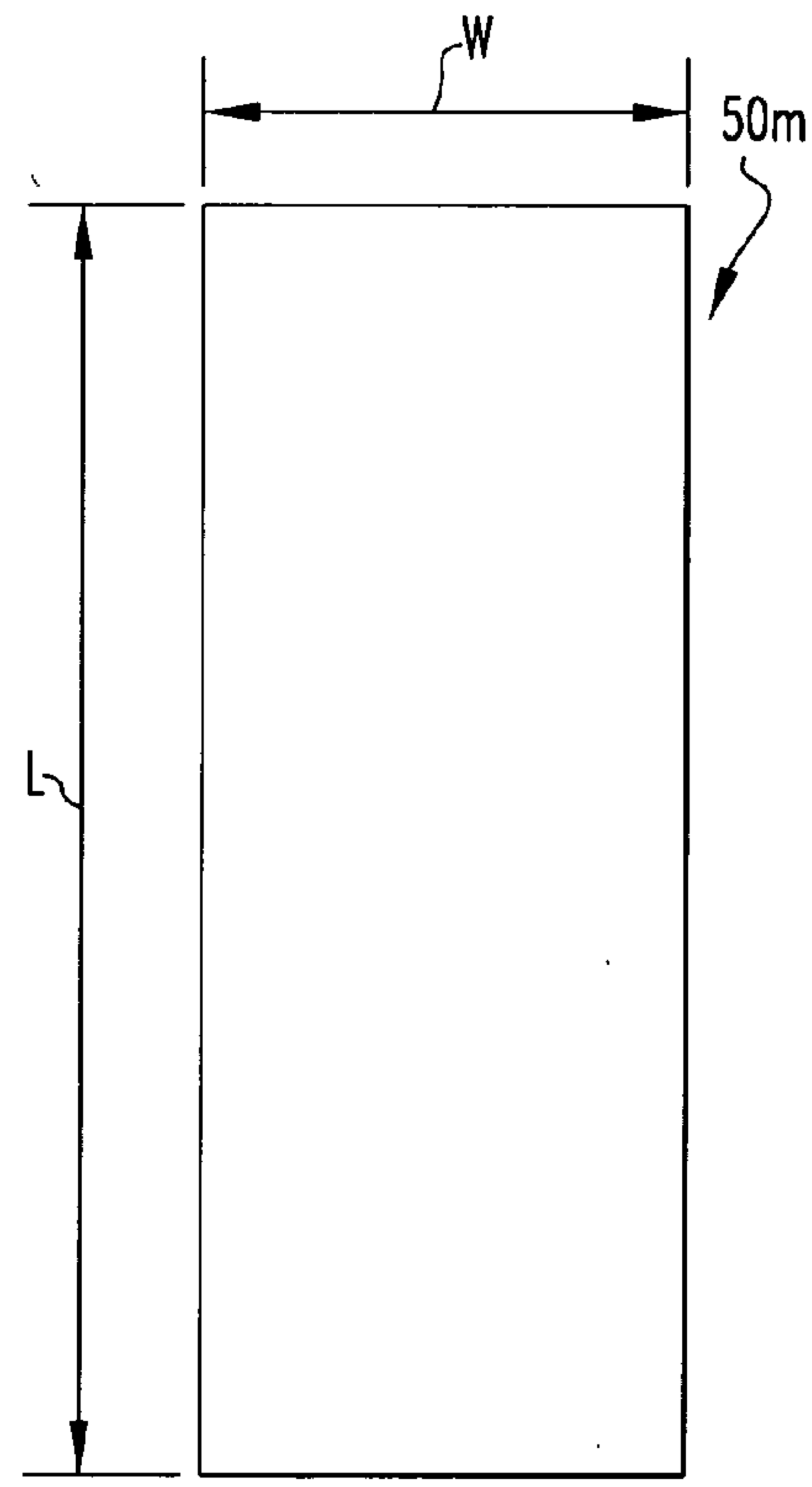


FIG.14

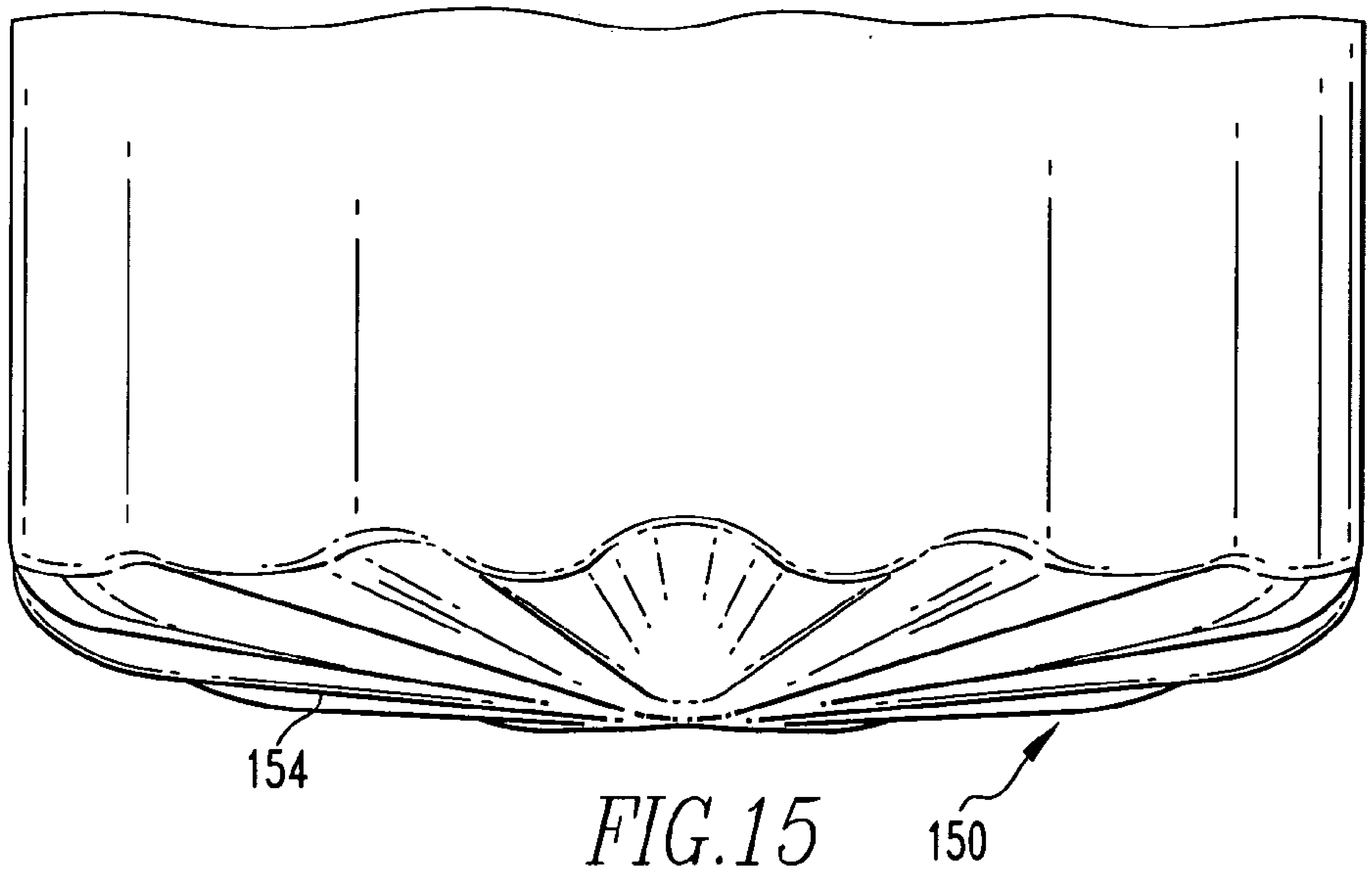


FIG.15

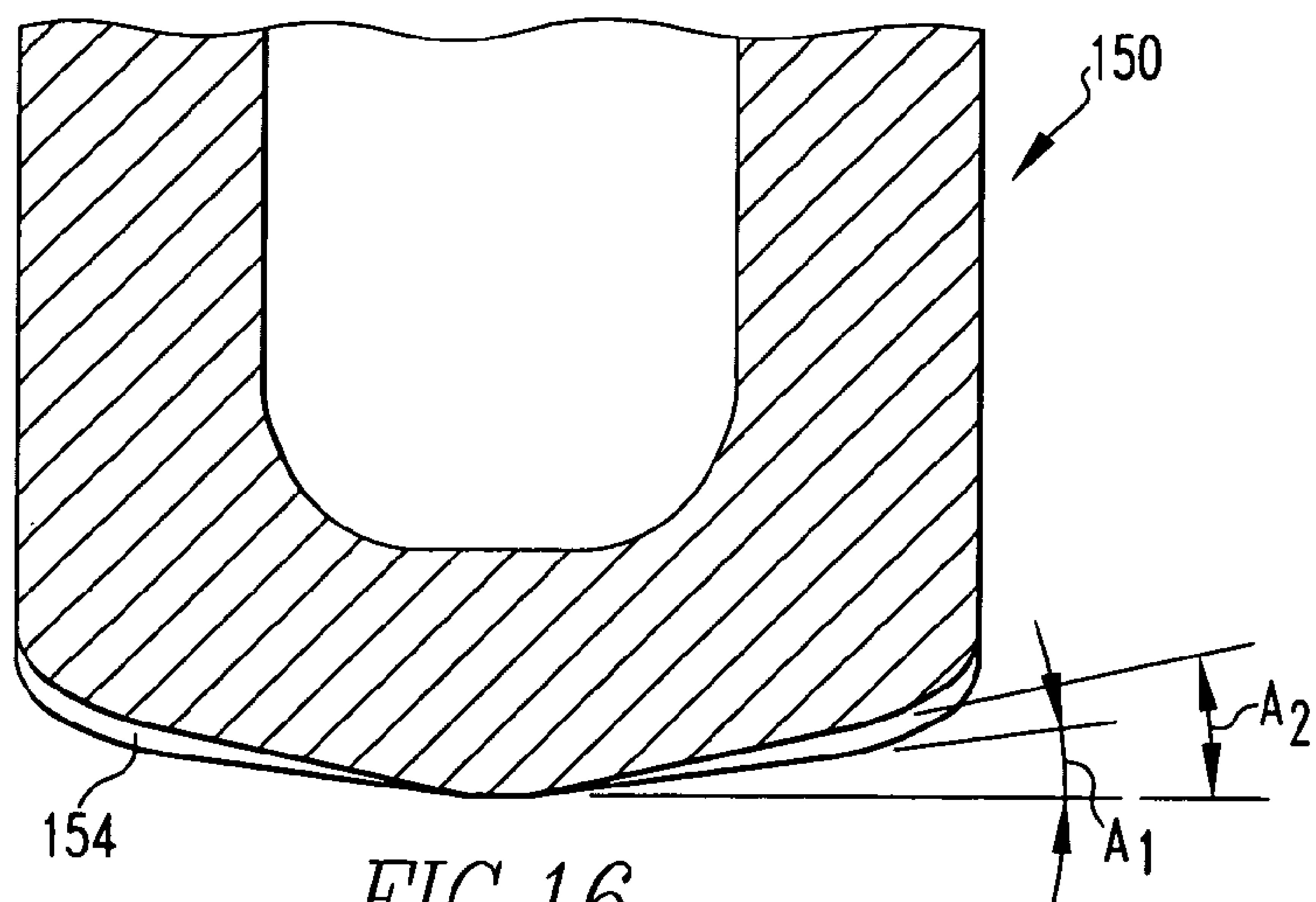


FIG.16

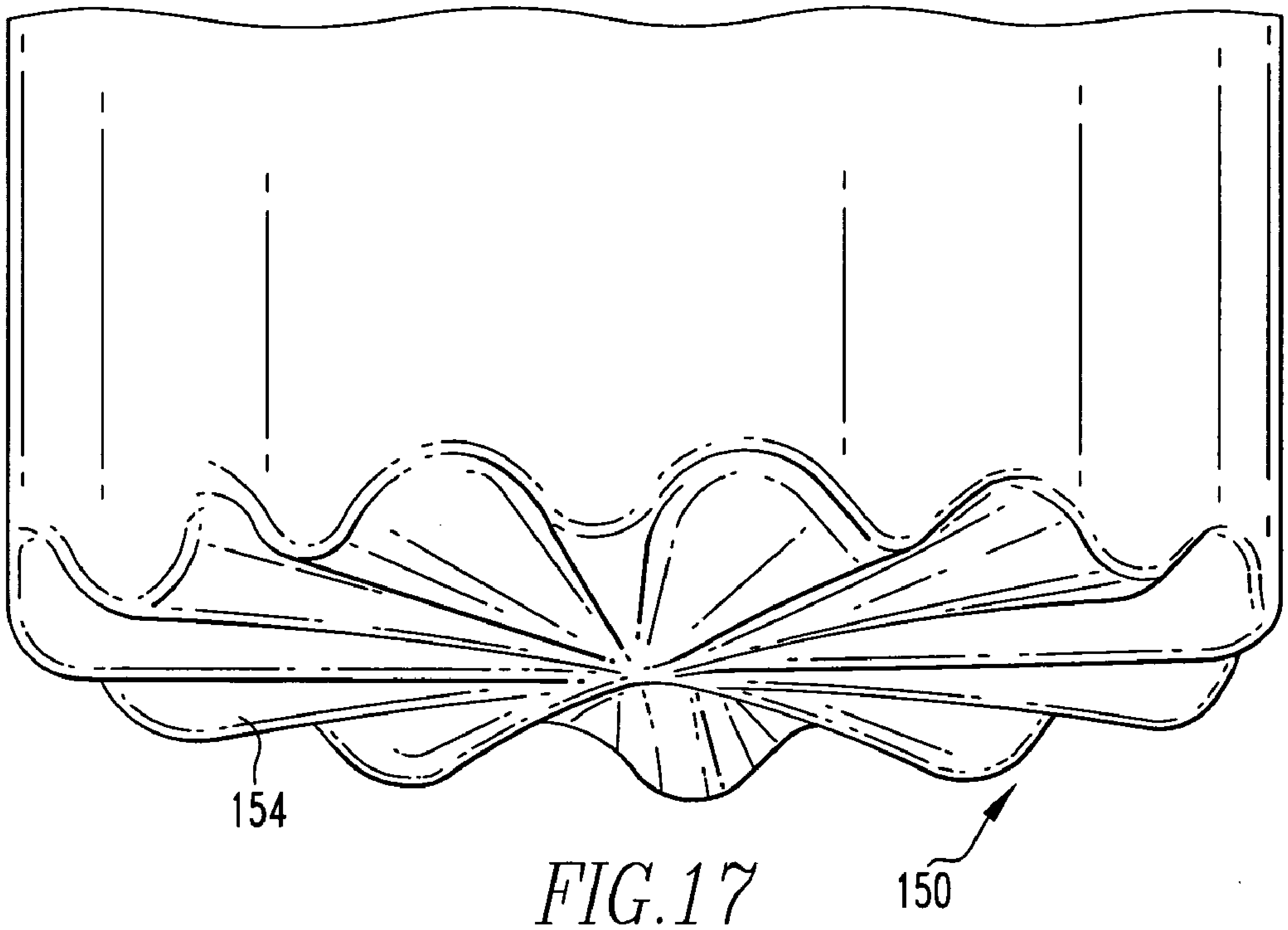


FIG.17

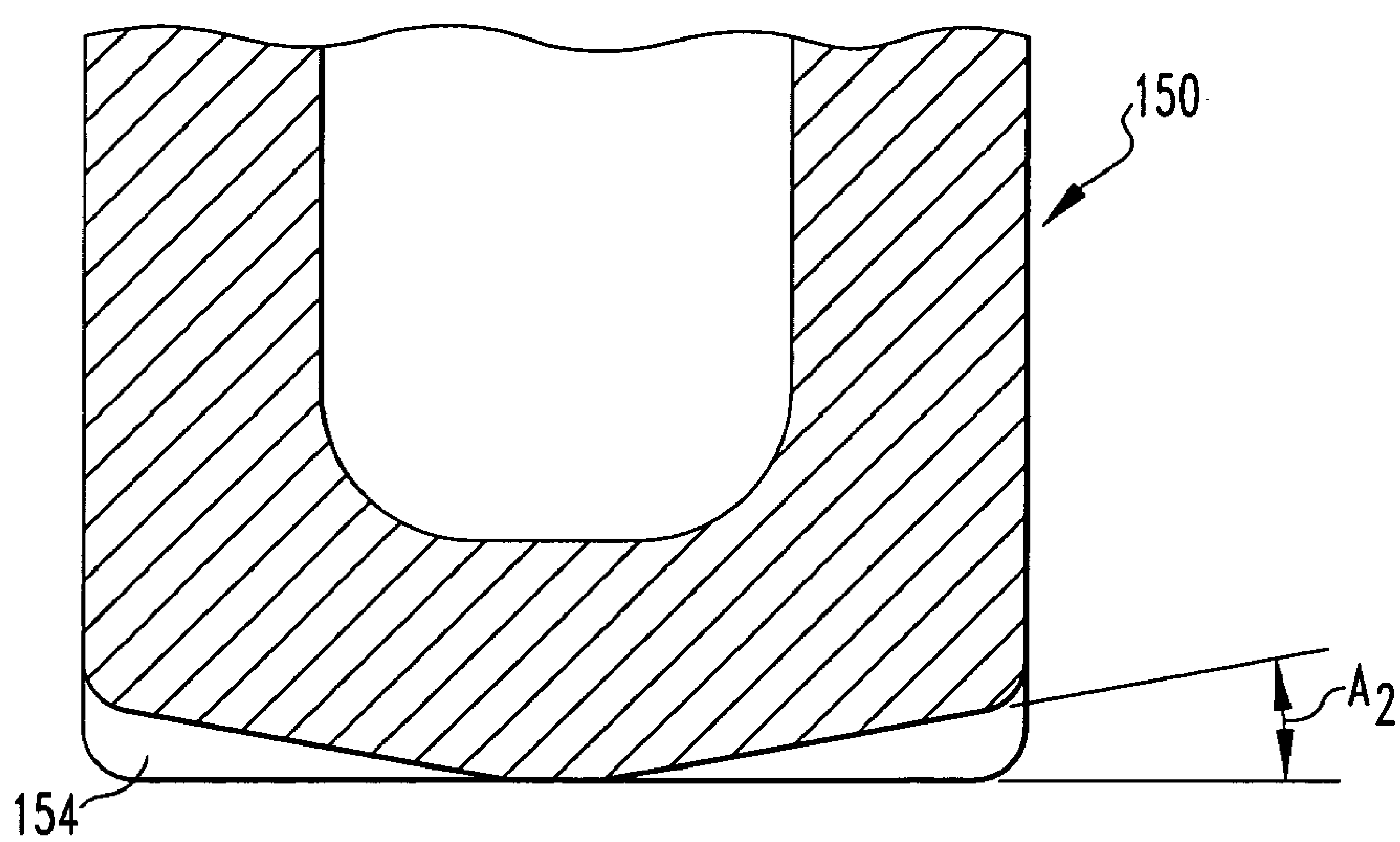


FIG.18

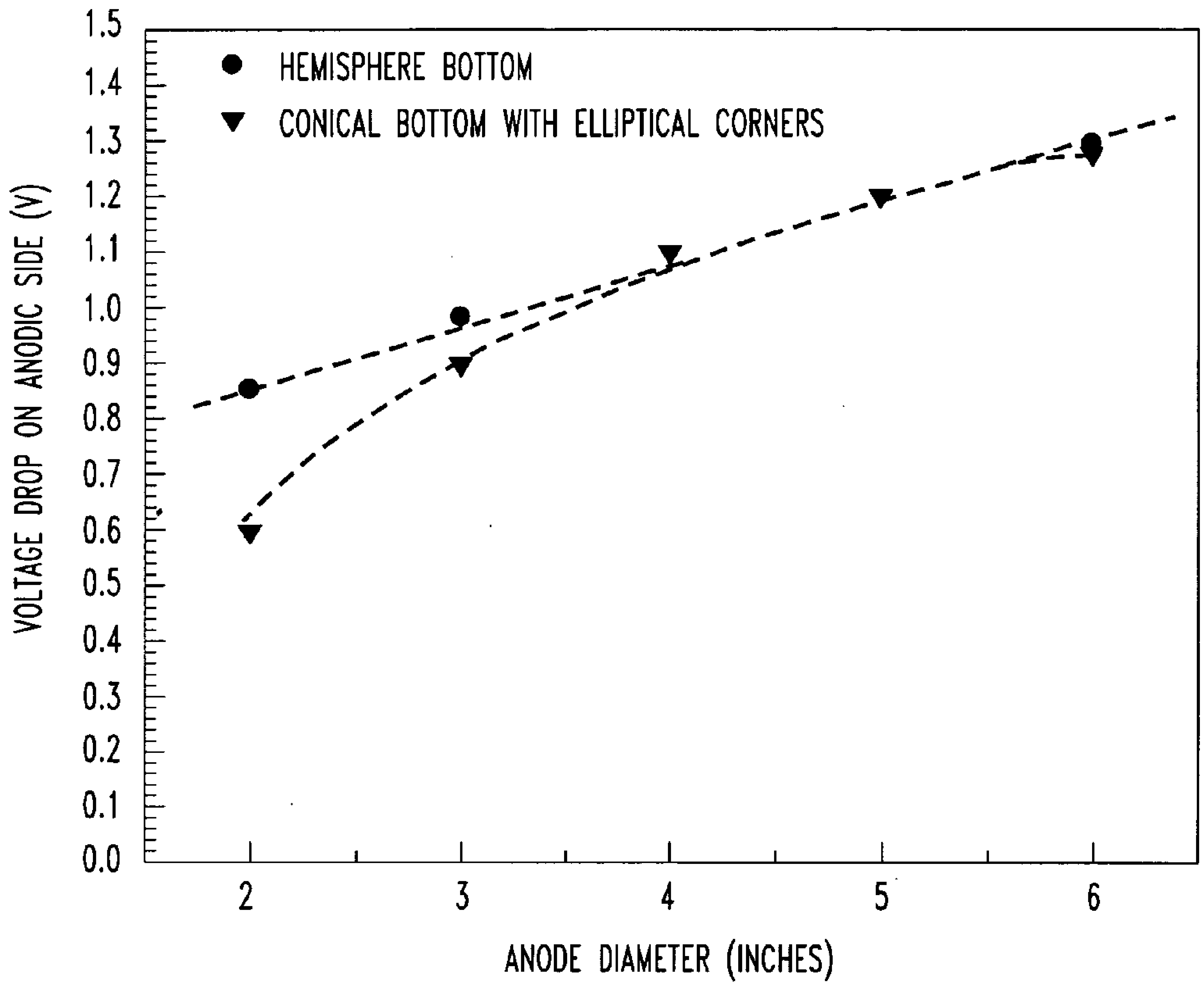

HEMISPHERE BOTTOM
CONICAL BOTTOM WITH ELLIPTICAL CORNERS
VOLTAGE DROP ON ANODIC SIDE (V)
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
2
3
4
5
6
ANODE DIAMETER (INCHES)

FIG.19

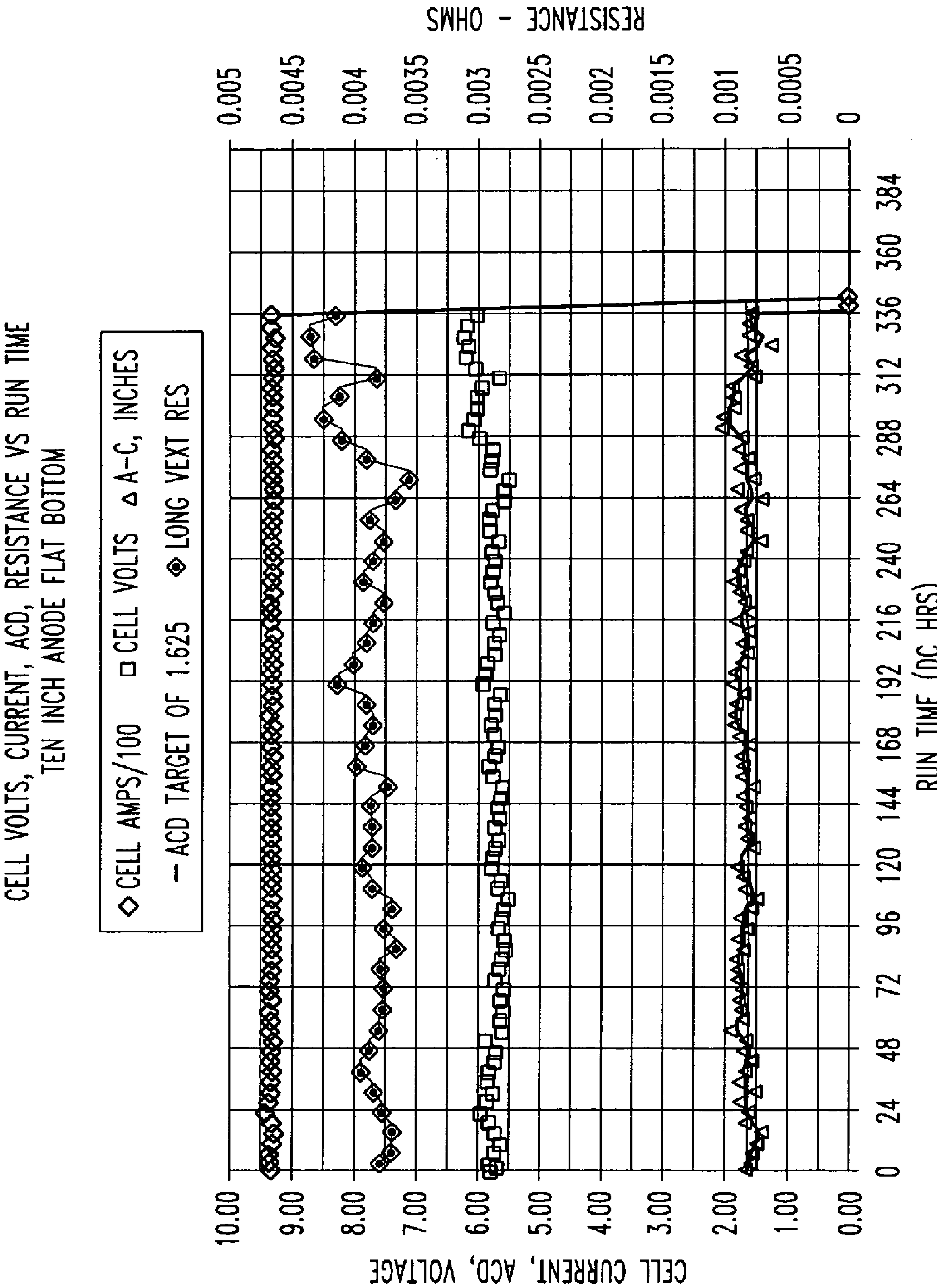

CELL VOLTS, CURRENT, ACD, RESISTANCE VS RUN TIME
TEN INCH ANODE FLAT BOTTOM
CELL AMPS/100
CELL VOLTS
A-C, INCHES
ACD TARGET OF 1.625
LONG VEXT RES
CELL CURRENT, ACD, VOLTAGE
RESISTANCE - OHMS
RUN TIME (DC HRS)
10.00
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
0.005
0.0045
0.004
0.0035
0.003
0.0025
0.002
0.0015
0.001
0.0005
0
0
24
48
72
96
120
144
168
192
216
240
264
288
312
336
360
384

FIG.20

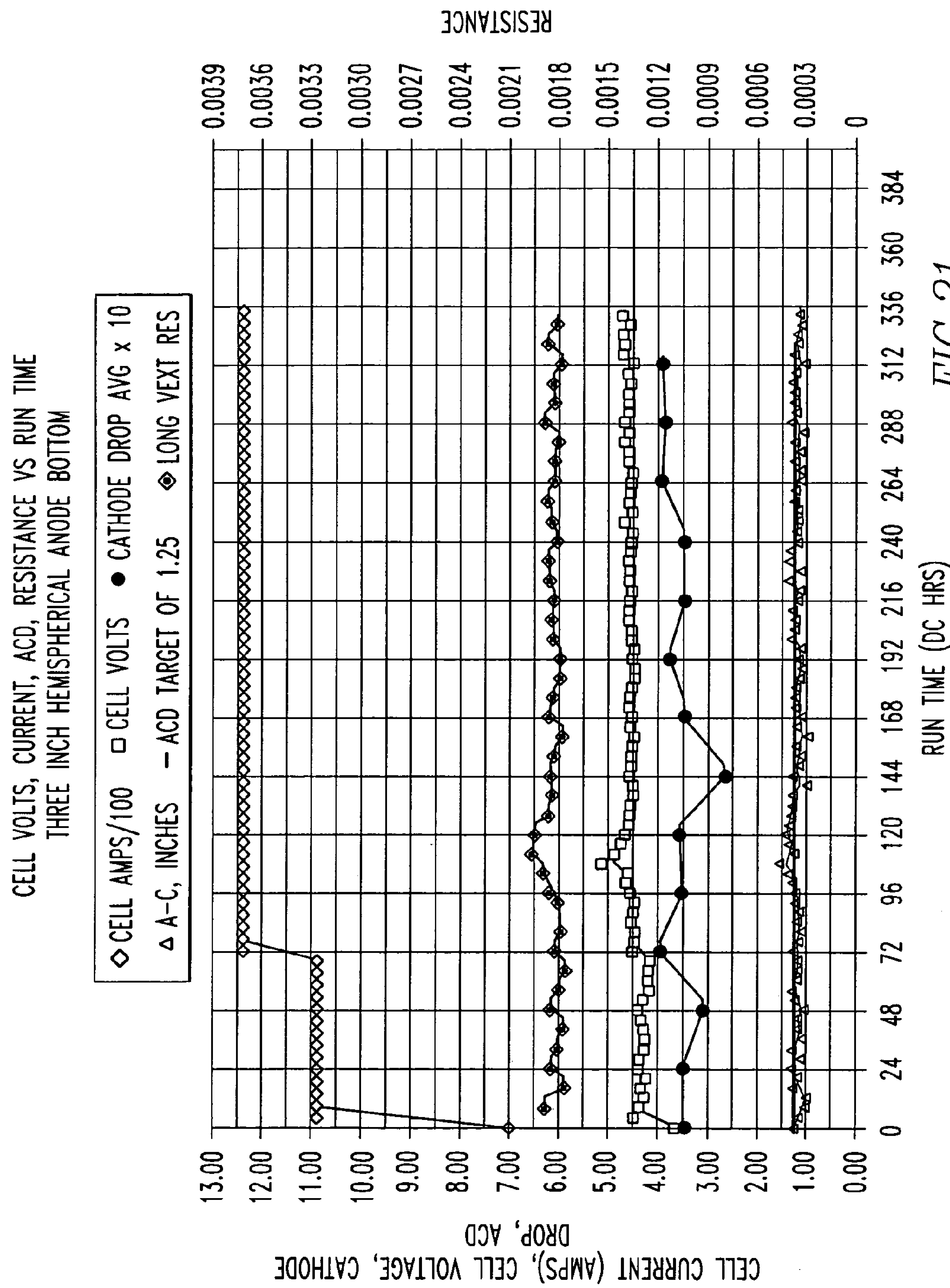

CELL VOLTS, CURRENT, ACD, RESISTANCE VS RUN TIME
THREE INCH HEMISPHERICAL ANODE BOTTOM
◇ CELL AMPS/100
□ CELL VOLTS
● CATHODE DROP AVG x 10
△ A–C, INCHES
— ACD TARGET OF 1.25
◈ LONG VEXT RES
CELL CURRENT (AMPS), CELL VOLTAGE, CATHODE DROP, ACD
RESISTANCE
RUN TIME (DC HRS)
13.00
12.00
11.00
10.00
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
0.0039
0.0036
0.0033
0.0030
0.0027
0.0024
0.0021
0.0018
0.0015
0.0012
0.0009
0.0006
0.0003
0
0
24
48
72
96
120
144
168
192
216
240
264
288
312
336
360
384

FIG. 21

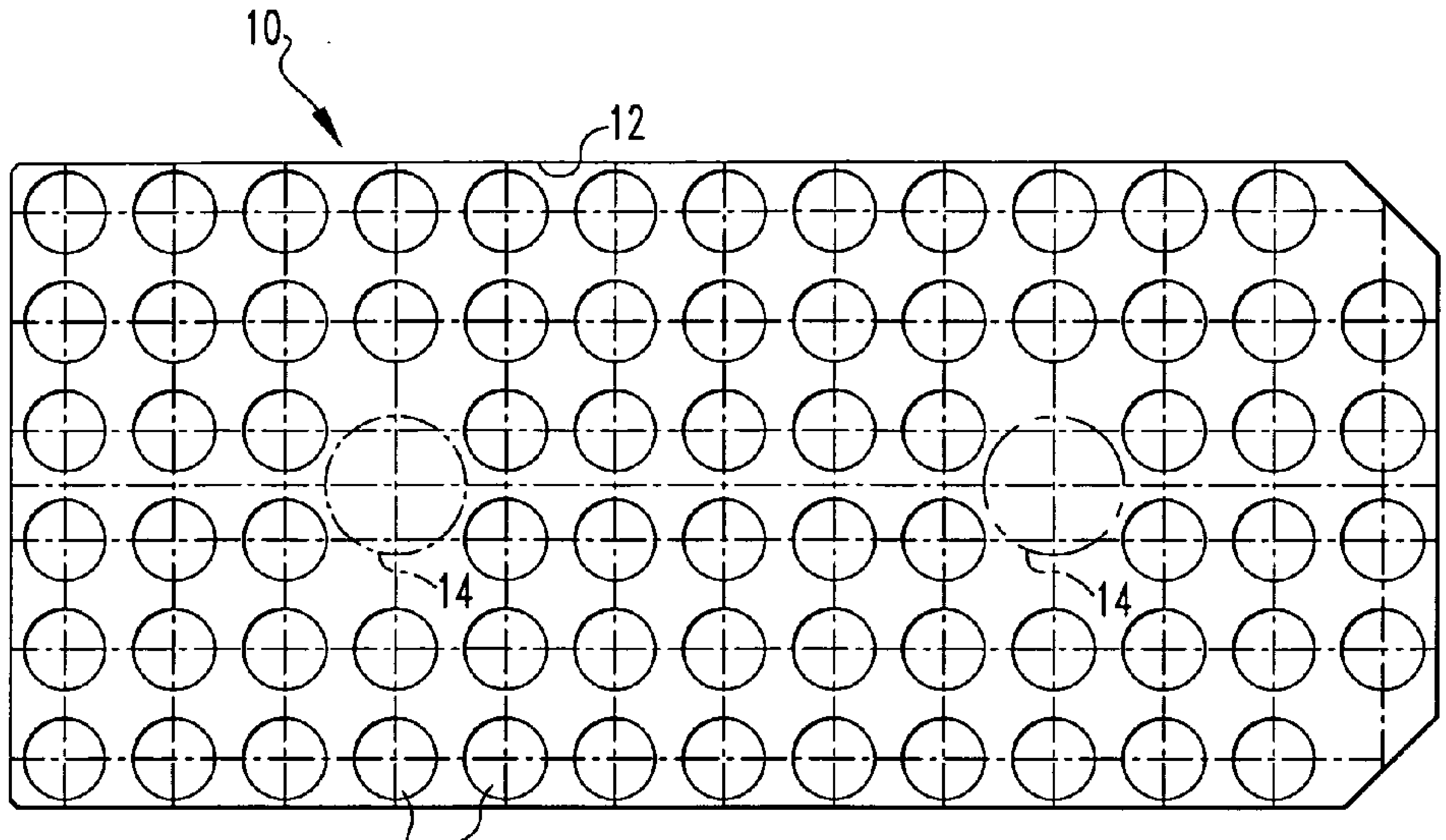


FIG. 22

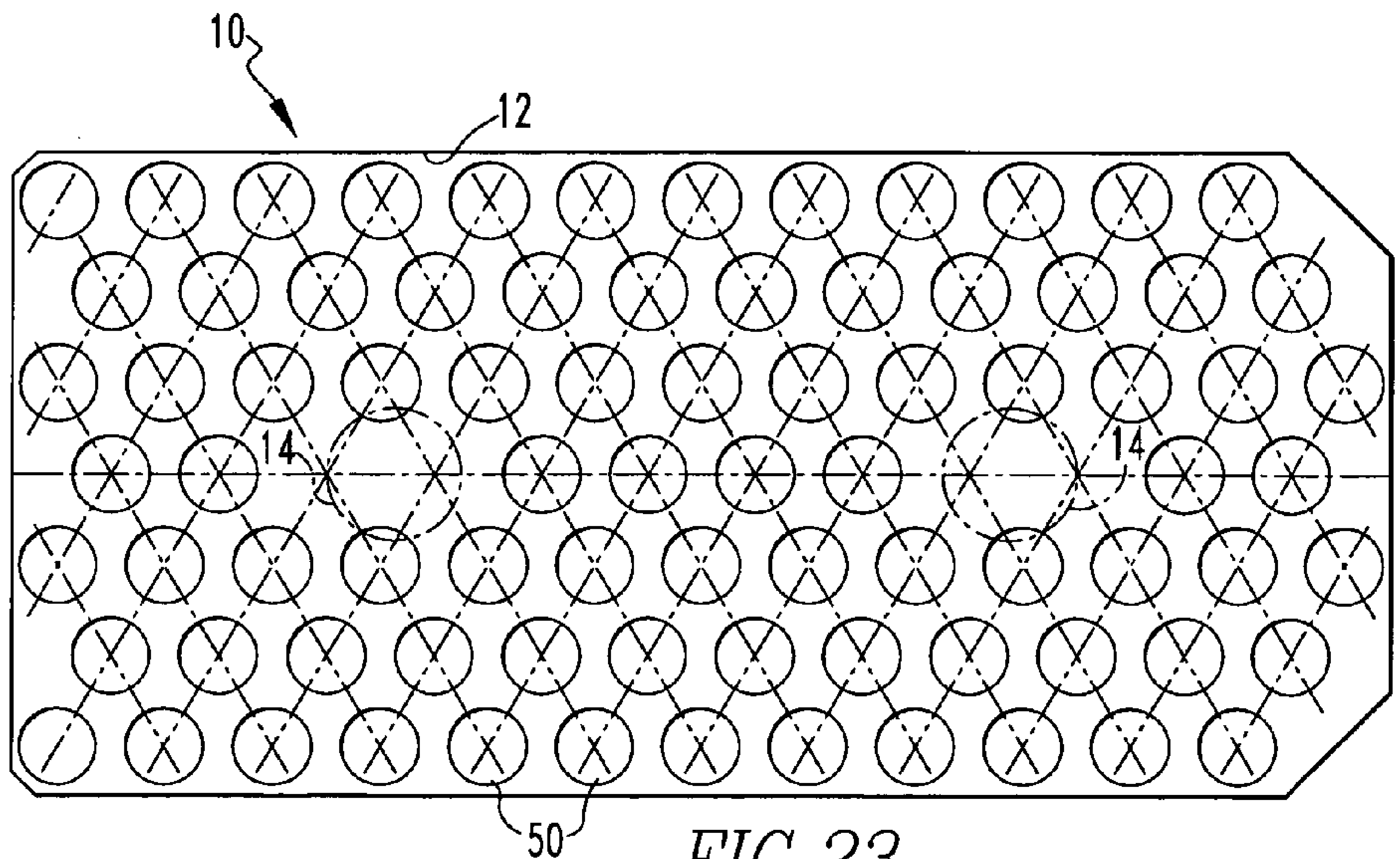


FIG. 23

INERT ANODE DESIGNS FOR REDUCED OPERATING VOLTAGE OF ALUMINUM PRODUCTION CELLS

FIELD OF THE INVENTION

[0001] The present invention relates to inert anodes useful for the electrolytic production of aluminum, and more particularly relates to inert anode designs which result in reduced operating voltages of aluminum production cells.

BACKGROUND OF THE INVENTION

[0002] The energy and cost efficiency of aluminum smelting can be significantly reduced with the use of inert, non-consumable and dimensionally stable anodes. Replacement of traditional carbon anodes with inert anodes should allow a highly productive cell design to be utilized, thereby reducing capital costs. Significant environmental benefits are also possible because inert anodes produce no CO_2 or CF_4 emissions. Some examples of inert anode compositions are provided in U.S. Pat. Nos. 4,374,050, 4,374,761, 4,399,008, 4,455,211, 4,582,585, 4,584,172, 4,620,905, 5,794,112, 5,865,980, 6,126,799, 6,217,739, 6,372,119, 6,416,649, 6,423,204 and 6,423,195, assigned to the assignee of the present application. These patents are incorporated herein by reference.

SUMMARY OF THE INVENTION

[0003] The present invention provides inert anode designs, which reduce operating voltages in electrolytic aluminum production cells.

[0004] An aspect of the present invention is to provide an inert anode for use in an electrolytic aluminum production cell. The inert anode comprises a bottom surface including a region that is upwardly sloped from an interior portion to an exterior portion of the inert anode, wherein the upwardly sloped region has a bubble release angle of up to about 30 degrees.

[0005] Another aspect of the present invention is to provide an inert anode for use in an electrolytic aluminum production cell. The inert anode comprises a substantially conical bottom surface having a preferred bubble release angle of from about 5 to about 30 degrees.

[0006] A further aspect of the present invention is to provide an array of inert anodes for use in an electrolytic aluminum production cell. The array comprises a plurality of inert anodes comprising a bottom surface including a region that is upwardly sloped from an interior portion to an exterior portion of the inert anode, wherein the upwardly sloped region has a bubble release angle of up to about 30 degrees.

[0007] Another aspect of the present invention is to provide an electrolytic aluminum production cell comprising a molten salt bath comprising an electrolyte and aluminum oxide; a cathode; and an inert anode comprising a bottom surface including a region that is upwardly sloped from an interior portion to an exterior portion of the inert anode, wherein the upwardly sloped region has a bubble release angle of up to about 30 degrees.

[0008] A further aspect of the present invention is to provide a method of operating an aluminum production cell. The method comprises passing current between an inert anode and a cathode through a molten salt bath comprising an electrolyte and aluminum oxide; and controlling flow of oxygen bubbles generated at a surface of the inert anode by providing the inert anode with a bottom surface including a region that is upwardly sloped from an interior portion to an exterior portion of the inert anode, wherein the upwardly sloped region has a bubble release angle of up to about 30 degrees.

[0009] These and other aspects of the present invention will be more apparent from the following description.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] **FIG. 1** is a partially schematic sectional view of an electrolytic aluminum production cell including an inert anode having a generally conical bottom surface with a controlled bubble release angle in accordance with an embodiment of the present invention.

[0011] **FIG. 2** is a photograph of a consumable carbon anode in an electrolytic aluminum production cell, illustrating generation of relatively large carbon dioxide bubbles on the exterior surface of the carbon anode during operation of the cell.

[0012] **FIG. 3** is a photograph of an inert anode in an electrolytic aluminum production cell, illustrating the generation of relatively small oxygen bubbles on the exterior surface of the inert anode during operation of the cell.

[0013] **FIG. 4** is a histogram of gas bubble number versus gas bubble diameter, illustrating different gas bubble size distributions for gas bubbles generated by a carbon anode and gas bubbles generated by an inert anode during operation of electrolytic aluminum production cells.

[0014] **FIG. 5** is a longitudinal sectional view of an inert anode in accordance with an embodiment of the present invention.

[0015] **FIG. 6*a*** is a longitudinal sectional view of the bottom portion of an inert anode having a flat bottom surface.

[0016] **FIGS. 6*b*-6*f*** are longitudinal sectional views of the lower portions of inert anodes having angled bottom surfaces.

[0017] **FIG. 7** is graph of voltage versus inert anode bottom surface slope, illustrating reduced voltages for certain slope angles.

[0018] **FIGS. 8*a*-8*c*** are longitudinal sectional views of the bottom portions of inert anodes in accordance with various embodiments of the present invention.

[0019] **FIG. 9** is a longitudinal sectional view of the bottom portion of an inert anode in accordance with another embodiment of the present invention.

[0020] **FIG. 10** is a longitudinal sectional view of the bottom portion of an inert anode in accordance with a further embodiment of the present invention.

[0021] **FIG. 11** illustrates an inert anode having a circular cross section in accordance with an embodiment of the present invention.

[0022] **FIG. 12** illustrates an inert anode having a generally elliptical or ovular cross section in accordance with another embodiment of the present invention.

[0023] **FIG. 13** illustrates an inert anode having an elongated cross section in accordance with a further embodiment of the present invention.

[0024] **FIG. 14** illustrates an inert anode having a rectangular cross section in accordance with another embodiment of the present invention.

[0025] **FIGS. 15 and 16** are isometric and longitudinal sectional views, respectively, of an inert anode having a non-uniform wavy bottom surface in accordance with an embodiment of the present invention.

[0026] **FIGS. 17 and 18** are isometric and longitudinal sectional views, respectively, of an inert anode having a non-uniform wavy bottom surface in accordance with another embodiment of the present invention.

[0027] **FIG. 19** is a graph of voltage versus inert anode diameter, illustrating lower voltages for smaller anode diameters.

[0028] **FIG. 20** is a graph of cell operation parameters versus cell operation time for an aluminum production cell with a single inert anode having a diameter of 10 inches.

[0029] **FIG. 21** is a graph of cell operation parameters versus cell operation time for an aluminum production cell with an array of twelve inert anodes having diameters of 3 inches.

[0030] **FIG. 22** is a top view of an array of inert anodes in an electrolytic aluminum production cell in accordance with an embodiment of the present invention.

[0031] **FIG. 23** is a top view of an array of inert anodes in an electrolytic aluminum production cell in accordance with another embodiment of the present invention.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0032] **FIG. 1** schematically illustrates an electrolytic cell for the production of aluminum. The cell includes an inner crucible **10** inside a protection crucible **20**. A cryolite bath **30** is contained in the inner crucible **10**, and a cathode **40** is provided in the bath **30**. An inert anode **50** is positioned in the bath **30**. An alumina feed tube **60** extends partially into the inner crucible **10** above the bath **30**. The cathode **40** and inert anode **50** are separated by a distance **70** known as the anode-cathode distance (ACD). Commercial purity aluminum **80** produced during a run is deposited on the cathode **40** and on the bottom of the crucible **10**. Alternatively, the cathode may be located at the bottom of the cell, and the aluminum produced by the cell forms a pad at the bottom of the cell.

[0033] **FIGS. 2 and 3** illustrate differences in gas bubble generation during operation of an electrolytic aluminum production cell using a carbon anode (**FIG. 2**) versus a cell using an inert anode (**FIG. 3**). The photographs of **FIGS. 2 and 3** were taken from a see-in cell operated with conventional Hall process electrolyte. The see-in cell is a cell contained in a quartz vessel with proper lighting so that the electrochemical operation can be observed. **FIG. 2** shows the formation of relatively large CO_2 bubbles, which average from 0.5 to 6 mm in diameter, evolving from a cylindrical 12.5 mm diameter carbon based electrode at a nominal current of 4 amperes. **FIG. 3** shows bubble formation on an inert anode comprising an Fe—Ni-oxide/Cu—Ag cermet material having the same size as the carbon anode at the same current. Stop action photography indicates relatively small bubble sizes on the cermet anode, averaging from about 0.1 to 0.5 mm.

[0034] **FIG. 4** is a graph of gas bubble number vs. gas bubble diameter for gas bubbles generated during operation of electrolytical aluminum production cells by a carbon anode as illustrated in **FIG. 2** and an inert anode as illustrated in **FIG. 3**. The bubble size distribution generated by the inert anode is substantially smaller than the carbon anode bubble size distribution.

[0035] A difference between conventional carbon anodes and ceramic or cermet inert anode materials is the differing contact angle measured between the electrolyte and the anode materials. The measured contact angle for the inert anode angle material is less than 10 degrees, indicating high wetting between the inert anode and the electrolyte. The contact angle for the carbon-based material is about 127 degrees, indicating low wetting between the electrolyte and the carbon anode. Bubble layer thickness and bubble volume fraction on the bottom of the inert anode is significantly affected by the generation of an increased number of smaller bubbles. Bubble layer build-up on inert anodes can have the disadvantage of significantly increasing the operating voltage of a cell.

[0036] **FIG. 5** is a longitudinal sectional view of an inert anode **50** in accordance with an embodiment of the present invention. The inert anode **50** has a generally cylindrical shape with an exterior wall **51** and an interior wall **52**. The inert anode **50** is attached to a mechanical support assembly (not shown). The inert anode **50** has an angled bottom surface **54** and includes a lower tip **56** and a curved shoulder **58**. The angled bottom surface **54** defines a bubble release angle A which may range up to about 30 degrees. For example, the bubble release angle A may range from 2 to 20 degrees, preferably from 5 to 15 degrees. In a particularly preferred embodiment, the bubble release angle A is from about 8 to about 10 or 12 degrees. In the embodiment shown in **FIG. 5**, the angled bottom surface **54** has a conical shape and the bubble release angle A remains substantially constant around the circumference of the bottom surface **54**. Alternatively, as more fully described below, the angled bottom surface **54** may comprise a non-uniform or wavy surface. Furthermore, although the angled bottom surface **54** shown in **FIG. 5** has a substantially flat cross section, the bottom surface **54** may alternatively be curved or faceted.

[0037] As shown in **FIG. 5**, the inert anode **50** has a height H typically ranging from about 4 to about 15 inches, preferably from about 6 to about 12 inches. The inert anode **50** also has a diameter D which, in accordance with an embodiment of the present invention, is controlled within certain ranges in order to increase operation efficiency of aluminum production cells. The diameter D is preferably less than 10 inches. For example, diameter D of the inert anode **50** may typically range from about 1.5 to about 6 inches, preferably from about 2 to about 4 inches.

[0038] Various bubble release angles A were studied in order to determine optimal angles of the bottom surface **54** for reduced cell voltage and improved operation efficiency. Cylindrical inert anodes having diameters of 3 inches and angled bottom surfaces were prepared as shown in **FIGS. 6***a*-**6***f*. Each inert anode was made of a cermet material comprising 95 weight percent of an NiZnFe oxide phase and 5 weight percent of a CuAg metal phase. The inert anode **50***a* shown in **FIG. 6***a* had a flat bottom surface, while the inert anodes shown in **FIGS. 6***b*-**6***f* had angled bottom surfaces ranging from 2 to 30 degrees. Specifically, the inert anodes **50***b*-**50***f* as shown in **FIGS. 6***b*-**6***f* had bubble release angles A of 2, 5, 8, 15 and 30 degrees, respectively.

[**0039**] The anodes shown in **FIGS. 6***a*-**6***f* were tested in a bench scale aluminum production cell. Each anode was mounted in an alumina tube with only its bottom portion exposed. The anodes were pre-heated slowly before immersion into the alumina-saturated cryolite bath with a NaF/AlF_3 ratio from 1.00 to 1.20 at a temperature range from 960 to 980° C. The anode was connected to a DC power supply/potentiostat. The cathode comprised a pool of aluminum on a TiB_2 plate which was connected to a DC power supply/potentiostat through a carbon crucible and Inconel retort. Voltage drops were monitored by placing volt-meters across different sections of the cell. Overpotential was measured by current interruption. Tests were carried out under constant current mode with current density from 0.001 to 3.5 A/cm^2.

[**0040**] **FIG. 7** is a graph of voltage drop on the anodic side at a current density of 1 A/cm^2 versus bubble release angle for the anodes shown in **FIGS. 6***a*-**6***f*. As shown in **FIG. 7**, the voltage drop of the flat bottomed anode is well over 2 volts, while the voltage drops of the sloped anodes are below 1.8 volts. The lowest voltage drop (below 1 volt) is achieved with the anode having a bubble release angle of 8 degrees. As demonstrated in **FIG. 7**, by controlling the bubble release angle A, cell voltage may be significantly decreased, thereby increasing operation efficiency.

[**0041**] **FIGS. 8***a*-**8***c* are longitudinal sectional views of the bottom portions of inert anodes in accordance with various embodiments of the present invention. The inert anode **50** shown in **FIG. 8***a*, which is similar to the anode shown in **FIG. 5**, includes a cone-shaped angled bottom surface **54** defining a pointed lower tip **56**. A curved shoulder **58** is provided between the bottom surface **54** and the exterior wall **51**. The inert anode **50***g* shown in **FIG. 8***b* has an angled bottom surface **54** with a slightly rounded lower tip **56***a*. An angled shoulder **58***a* is formed at the intersection of the bottom surface **54** and exterior wall **51**. The inert anode **50***h* shown in **FIG. 8***c* includes a bottom surface **54** with a slightly rounded lower tip **56***a* and a curved shoulder **58**.

[**0042**] The curved shoulder **58** shown in the embodiments of **FIGS. 5, 8***a* and **8***c* may be provided with a desired cross sectional shape, such as elliptical, circular, ovular or the like. The shape of the curved shoulder **58** may be selected such that a substantially uniform current density is achieved from the lower portion of the inert anode. In one embodiment, the curved shoulder **54** may have a substantially elliptical shape. Every point on an ellipse has the characteristic that the sum of the distances from two fixed points or foci to the point is constant. The line connecting the foci defines an axis of symmetry, the major axis. The designations a, b, and c may be used to represent the semimajor axis, the semiminor axis, and the half focal separation or the distance from the center of the ellipse to one focus, respectively. One way to describe the shape of an elipse is through eccentricity, e, which may vary from 0 to 1. The relation between eccentricity e and the ratio b/a is: $e^2=1-b^2/a^2$. The ratio of b/a may range from about 0.8 to 0.2, for example, a b/a ratio of 0.35 may be used.

[**0043**] The slightly rounded lower tip **56***a* shown in **FIGS. 8***b* and **8***c* may have a curved cross sectional shape, such as circular, elliptical or the like. For example, where the inert anode has a diameter D of 3 inches, the lower tip **56***a* may have a radius of curvature of from about 0.5 to about 2 inches.

[**0044**] **FIG. 9** is a longitudinal sectional view of the bottom portion of an inert anode **50***i* in accordance with another embodiment of the present invention. The inert anode **50***i* shown in **FIG. 9** includes a sloped lower surface **54***a* having a generally ellipsoidal cross section. The ellipsoidal lower surface **54***a* defines the lowermost point **56***b* of the inert anode. The inert anode **50***i* shown in **FIG. 9** also includes a curved shoulder **58**.

[**0045**] **FIG. 10** is a longitudinal sectional view of the bottom portion of an inert anode **50***j* in accordance with a further embodiment of the present invention. The inert anode **50***j* includes a substantially hemispherical bottom surface **54***b* defining a lowermost point **56***c*. A curved shoulder **50***b* is defined at the intersection of the hemispherical bottom surface **54***b* and the vertical exterior wall **51**.

[**0046**] **FIG. 11** illustrates an inert anode **50** having a circular cross section with a diameter D in accordance with an embodiment of the present invention.

[**0047**] **FIG. 12** illustrates an inert anode **50***k* having a generally elliptical or ovular cross section in accordance with an embodiment of the present invention. The inert anode **50***k* has a short dimension X that may typically range from 1 to 6 inches, and a long dimension Y that may typically range from 2 to 10 inches or more.

[**0048**] **FIG. 13** illustrates an inert anode **50***l* having an elongated cross section in accordance with a further embodiment of the present invention. The inert anode **50***l* has a width W that may typically range from 1 to 6 inches, and a length L that may typically range from 3 to 10 inches or more. In one embodiment, the length L may be selected such that the inert anode **50***l* extends across substantially the entire width or length of the aluminum production cell.

[**0049**] **FIG. 14** illustrates an inert anode **50***m* having a rectangular cross section in accordance with another embodiment of the present invention. The inert anode **50***m* has a width W that may typically range from 1 to 6 inches, and a length L that may typically range from 3 to 10 inches or more. In one embodiment, the length L may be selected such that the inert anode **50***m* extends across substantially the entire width or length of the aluminum production cell.

[**0050**] In one embodiment, the inert anodes have a shape that is substantially symmetrical about a central axis of rotation. For example, each of the inert anodes shown in **FIGS. 6***b*-**6***f*, **8***a*-**8***c*, **9** and **10** are symmetrical about the central longitudinal axis of the anode. Alternatively, the inert anode shape may be non-symmetrical about a central axis of rotation. In this case, the bottom surface of the inert anode may be non-uniform, e.g., wavy, grooved, etc.

[0051] FIGS. **15-18** illustrate the bottom surfaces of anodes in accordance with embodiments of the present invention having non-uniform or wavy surfaces. **FIG. 15** is an isometric view and **FIG. 16** is a longitudinal sectional view of an inert anode having a wavy bottom **154**. In this embodiment, the bottom surface **154** is non-symetrical about an axis of rotation defined by the central longitudinal axis of the inert anode **150**. The bottom surface **154** has a minimum bubble release angle A_1, and a maximum bubble release angle A_2, with additional bubble release angles between the minimum and maximum angles. The minimum bubble release angle A_1 may range from zero to 20 degrees, typically from 1 to 15 degrees. The maximum bubble release angle A_2 may range up to about 30 degrees or higher. For example, the maximum bubble release angle A_2 may range from 2 to 20 degrees, typically from 5 to 15 degrees. In the embodiment shown in **FIGS. 15 and 16**, the minimum bubble release angle A_1 is 8 degrees and the maximum bubble release angle A_2 is 12 degrees.

[0052] The embodiment shown in **FIGS. 17 and 18** is similar to the embodiment shown in **FIGS. 15 and 16**, except the minimum bubble release angle A_1 is zero degrees and the maximum bubble release angle A_2 is 10 degrees.

[0053] Tests were performed on 2-inch diameter, 3-inch diameter, 4-inch diameter, 5-inch diameter and 6-inch diameter inert anodes having 10 degree conical bottoms with elliptical shoulders as shown in **FIG. 8***c* and hemispherical bottoms as shown in **FIG. 10** were tested. **FIG. 19** is a graph of voltage drop on the anodic side at current density of 1 A/cm^2 versus inert anode diameter, illustrating significantly lower voltages for the smaller anode diameters.

[0054] Studies based on 10-inch diameter inert anodes versus smaller anodes showed a surprising increase in cell voltage, e.g., as much as 2.4 volts, for the larger versus smaller anodes. This difference was found to be due primarily to the high gas film thickness of the larger diameter anodes. Anode tests were conducted with multiple 3-inch anodes replacing one 10-inch anode. The results are illustrated in **FIGS. 20 and 21**. **FIG. 20** shows the operating characteristics of a 10-inch anode in a two week test. The anode cathode distance ACD was controlled to 1.625 inches. The operating current of 940 amperes, the cell voltage, and the cell resistance in ohms are shown in **FIG. 20**. The cell voltage during the test ranged from 5.75 to a little over 6 volts.

[0055] In comparison, as shown in **FIG. 21, a** cell fitted with twelve 3-inch anodes to replace the single 10-inch anode was operated at a higher current of from 1,080 to 1,240 amperes, and a voltage of from 4.3 to 4.6 volts. As illustrated in **FIG. 21**, the minimum ACD for the 3-inch anodes was lower. However, the bottom of the 3-inch anodes had a hemispherical shape. The effective ACD over the bottom surfaces of the anodes is equivalent to the 1.625 inch ACD used in the case of a flat bottom 10-inch anode. This further illustrates the beneficial effect of reduced anode size and controlled bottom geometry on cell voltage.

[0056] In accordance with the present invention, operation efficiency of inert anode aluminum production cells is improved. For example, the cells may be operated at voltages below 6 volts, preferably below 5.5 volts. In a particularly preferred embodiment, the cells are operated at voltages below 5 volts. The current density of the cells is also controlled, for example, within a range of from 0.5 to 1.5 $Amps/cm^2$.

[0057] Anode arrangement refers to the planar spatial distribution of anodes within the cell. In accordance with an embodiment of the present invention, the arrangement of anodes in a particular assembly may be optimized to develop the lowest cell voltage during operation. In addition to minimizing cell voltage in optimized arrangements, consideration has also been given to limiting the maximum surface normal current densities, the individual anode currents, and the electrical interference with adjacent anodes.

[0058] Optimized arrangements are designed such that the gas film resistance produces a linear voltage drop response in the current density ranges of interest. Operating at higher current densities will produce nonlinear gas film voltage drops, which will result in higher cell voltages. Additionally, the current emanating from the anodes sidewalls and the added surface area in the sidewalls are considered in the optimized arrangements. Optimized arrangements create a balance between anode sidewall currents and anode tip currents. Failure to create this balance may result in high cell voltages. The anodes can be arranged, for example, in either hexagonal distributions or square distributions, with uniform and non-uniform spacing. For each anode size being considered, a distribution may be defined which minimizes cell voltage. For a particular cell, with its size and current requirements, combinations of anode size and anode arrangement may be selected in order to yield the lowest possible cell voltage.

[0059] **FIG. 22** is a top view of an array of inert anodes **50** in an electrolytic aluminum production assembly **10** in accordance with an embodiment of the present invention. The assembly **10** has a sidewall **12**. Holes **14** are provided in order to connect an electrical bus (not shown) to the assembly **10**. In the embodiment shown in **FIG. 22**, the inert anodes are provided in an array having a square pattern, with a total of seventy-two 3-inch anodes in a cell having a length of 25.6 inches and a width of 54 inches. The spacing between adjacent anodes is about 1.2 inches.

[0060] **FIG. 23** is a top view of an array of inert anodes **50** in an electrolytic aluminum production assembly **10** having a sidewall **12** in accordance with another embodiment of the present invention. In the embodiment shown in **FIG. 23**, the inert anodes are provided in an array having a hexagonal pattern, with a total of eighty-two 3-inch diameter anodes in a cell having a length of 25.6 inches and a width of 54 inches. The spacing between adjacent anodes is about 1.2 inches.

[0061] The inert anodes of the present invention may be formed by techniques such as powder sintering, sol-gel processes, chemical processes, co-precipitation, slip casting and spray forming. The starting materials may be provided in the form of metal oxides, nitrates, halides and the like. For example, the inert anodes may be formed by powder techniques in which powders comprising metal oxides, such as nickel, iron, aluminum, zinc and/or cobalt oxides and any metal additives or dopants are pressed and sintered. The inert anode may comprise a monolithic component of such materials, or may comprise a coated substrate of such materials.

[0062] As a particular example, nickel oxide, iron oxide and optional aluminum oxide, zinc oxide or cobalt oxide starting powders, e.g., NiO, Fe_2O_3, M_2O_3, ZnO and/or CoO, may be blended in a mixer. The blended ceramic powders may be ground to a smaller size before being transferred to a furnace where they are calcined, e.g., for 0.1 to 12 hours at 1,050 to 1,250° C. The oxide mixture may be ground in a ball mill to an average particle size of approximately 10 microns. The fine oxide particles may be blended with a polymeric binder/plasticizer and water to make a slurry. If a cermet anode material is desired, metal powders such as Cu, Ag, Pt and/or Pd may be added to the oxide powder slurry. About 0.1-10 parts by weight of an organic polymeric binder may be added to 100 parts by weight of the oxide and optional metal particles. Some suitable binders include polyvinyl alcohol, acrylic polymers, polyglycols, polyvinyl acetate, polyisobutylene, polycarbonates, polystyrene, polyacrylates, and mixtures and copolymers thereof. The slurry may contain, e.g., about 60 weight percent solids and about 40 weight percent water. Spray drying the slurry produces dry agglomerates of the oxides, optional metals and binders. The spray dried material may be pressed, for example, at 10,000 to 40,000 psi, into the present anode shapes. A pressure of about 20,000 psi is particularly suitable for many applications.

[0063] The pressed shapes may be sintered in an oxygen-containing atmosphere such as air, or in argon/oxygen, nitrogen/oxygen, H_2/H_2O or CO/CO_2 gas mixtures, as well as nitrogen. Oxide sintering temperatures of about 1,200-1,650° C. may be suitable. For example, the furnace may be operated at about 1,350-1,550° C. for 2-4 hours. The sintering process burns out any polymeric binder from the anode shapes.

[0064] The inert anodes may be connected to suitable electrically conductive support members within an electrolytic metal production cell by means such as welding, brazing, mechanically fastening, cementing and the like.

[0065] The present inert anodes are particularly useful in electrolytic cells for aluminum production operated at temperatures in the range of about 800-1,000° C. A typical cell operates at a temperature of about 900-980° C., for example, about 930-970° C. An electric current is passed between the inert anodes and at least one cathode through a molten salt bath comprising an electrolyte and an oxide of the metal to be collected. In a preferred cell for aluminum production, the electrolyte comprises aluminum fluoride and sodium fluoride and the metal oxide is alumina. The weight ratio of sodium fluoride to aluminum fluoride is about 0.7 to 1.25, preferably about 1.0 to 1.20. The electrolyte may also contain calcium fluoride, lithium fluoride and/or magnesium fluoride.

[0066] Having described the presently preferred embodiments, it is to be understood that the invention may be otherwise embodied within the scope of the appended claims.

What is claimed is:

1. An inert anode for use in an electrolytic aluminum production cell, the inert anode comprising a bottom surface including a region that is upwardly sloped from an interior portion to an exterior portion of the inert anode, wherein the upwardly sloped region has a bubble release angle of up to about 30 degrees.

2. The inert anode of claim 1, wherein the bubble release angle is from about 2 to about 20 degrees.

3. The inert anode of claim 1, wherein the bubble release angle is from about 5 to about 15 degrees.

4. The inert anode of claim 1, wherein the bubble release angle is from about 8 to about 12 degrees.

5. The inert anode of claim 1, wherein the bubble release angle is about 10 degrees.

6. The inert anode of claim 1, wherein the inert anode includes a cross sectional dimension of from about 2 to about 6 inches.

7. The inert anode of claim 1, wherein the inert anode is substantially cylindrical and has a cross sectional diameter of less than 10 inches.

8. The inert anode of claim 1, wherein the inert anode is substantially cylindrical and has a cross sectional diameter of from about 2 to about 6 inches.

9. The inert anode of claim 1, wherein the bottom surface is substantially symmetrical about an axis of rotation defined by a central longitudinal axis of the inert anode.

10. The inert anode of claim 1, wherein the bottom surface is non-symmetrical about an axis of rotation defined by a central longitudinal axis of the inert anode.

11. The inert anode of claim 10, wherein the bottom surface defines a minimum bubble release angle and a maximum bubble release angle, the minimum bubble release angle is from zero to about 20 degrees, and the maximum bubble release angle is from about 2 to about 30 degrees.

12. The inert anode of claim 11, wherein the minimum bubble release angle is from about 1 to about 15 degrees, and the maximum bubble release angle is from about 5 to about 20 degrees.

13. The inert anode of claim 1, wherein the bottom surface includes a substantially straight portion defined by a longitudinal section of the inert anode.

14. The inert anode of claim 13, wherein the bubble release angle is measured from the substantially straight portion.

15. The inert anode of claim 1, wherein the bottom surface is substantially conical.

16. The inert anode of claim 1, wherein the bottom surface has a lowermost tip.

17. The inert anode of claim 16, wherein the lowermost tip is located at an axial center of the inert anode.

18. The inert anode of claim 16, wherein the lowermost tip is rounded.

19. The inert anode of claim 18, wherein the rounded tip has a radius of curvature of from about 0.5 to about 2 inches.

20. The inert anode of claim 1, wherein the bottom surface comprises a curved shoulder at an intersection of the bottom surface and a sidewall of the inert anode.

21. The inert anode of claim 20, wherein the curved shoulder has a substantially elliptical shape.

22. The inert anode of claim 20, wherein the curved shoulder has a substantially circular shape.

23. The inert anode of claim 1, wherein the inert anode has an elongated cross section having a length to width aspect ratio of from about 1.1:1 to about 50:1.

24. The inert anode of claim 1, wherein the inert anode has a substantially rectangular cross section.

25. The inert anode of claim 1, wherein the inert anode has a substantially elliptical cross section.

26. The inert anode of claim 1, wherein the inert anode has a substantially ovular cross section.

27. The inert anode of claim 1, wherein the inert anode comprises a ceramic phase including an oxide of at least one metal selected from Fe, Ni, Zn, Co and Al.

28. An inert anode for use in an electrolytic aluminum production cell, the inert anode comprising a substantially conical bottom surface having a bubble release angle of from about 5 to about 30 degrees.

29. The inert anode of claim 28, wherein the bubble release angle is from about 8 to about 12 degrees.

30. The inert anode of claim 28, wherein the bubble release angle is about 10 degrees.

31. The inert anode of claim 28, wherein the inert anode includes a cross sectional dimension of from about 2 to about 6 inches.

32. The inert anode of claim 28, wherein the bottom surface has a rounded lowermost tip.

33. The inert anode of claim 28, wherein the bottom surface comprises a curved shoulder at an intersection of the bottom surface and a sidewall of the inert anode.

34. The inert anode of claim 33, wherein the curved shoulder has a substantially elliptical shape.

35. The inert anode of claim 33, wherein the curved shoulder has a substantially circular shape.

36. An array of inert anodes for use in an electrolytic aluminum production cell, the array comprising a plurality of inert anodes comprising a bottom surface including a region that is upwardly sloped from an interior portion to an exterior portion of the inert anode, wherein the upwardly sloped region has a bubble release angle of up to about 30 degrees.

37. The array of claim 36, wherein the inert anodes are spaced apart by a distance of from zero to about 5 inches.

38. The array of claim 36, wherein the inert anodes are provided in a substantially square pattern.

39. The array of claim 36, wherein the inert anodes are provided in a substantially hexagonal pattern.

40. The array of claim 36, wherein the inert anodes have cross sectional dimensions of from about 2 to about 6 inches.

41. An electrolytic aluminum production cell comprising:

a molten salt bath comprising an electrolyte and aluminum oxide;

a cathode; and

an inert anode comprising a bottom surface including a region that is upwardly sloped from an interior portion to an exterior portion of the inert anode, wherein the upwardly sloped region has a bubble release angle of up to about 30 degrees.

42. The electrolytic aluminum production cell of claim 41, wherein the cell comprises an array including a plurality of the inert anodes.

43. A method of producing aluminum comprising:

passing current between an inert anode and a cathode through a molten salt bath comprising an electrolyte and aluminum oxide; and

controlling flow of oxygen bubbles generated at a surface of the inert anode by providing the inert anode with a bottom surface including a region that is upwardly sloped from an interior portion to an exterior portion of the inert anode, wherein the upwardly sloped region has a bubble release angle of up to about 30 degrees.

44. The method of claim 43, wherein the bubble release angle is from about 5 to about 15 degrees.

45. The method of claim 43, wherein the inert anode has a cross sectional diameter of from about 2 to about 6 inches.

46. The method of claim 43, wherein the cell is operated at a voltage of less than about 6 volts.

47. The method of claim 43, wherein the cell is operated at a voltage of less than about 5.5 volts.

48. The method of claim 43, wherein the cell is operated at a voltage of less than about 5 volts.

49. The method of claim 43, wherein the cell is operated at a current density of from about 0.5 to about 1.5 Amps/ cm^2.

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