

# UNITED STATES PATENT APPLICATION

## TITLE OF THE INVENTION

METHOD OF FORMING A SOLDERABLE SHRINK-FIT METAL CAP ON A CARBON BODY BY LOW-SUPERHEAT DIP CASTING, AND ELECTRODE ASSEMBLIES MADE THEREBY

## INVENTOR

Robert Karas, Lake Wales, Florida, United States of America.

## APPLICANT / ASSIGNEE

Robert Karas (individual). The sole inventor is the applicant; no assignment is of record.

## CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] Not Applicable.

## STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] Not Applicable.

## FIELD OF THE INVENTION

[0003] The present disclosure relates generally to electrically conductive connections to carbon and graphite bodies, and more particularly to methods of forming a solderable metallic terminal on an end of a carbon or graphite rod or electrode by briefly immersing the end in a pool of molten metal maintained at low superheat, such that a solidified, mechanically self-retaining, solderable metal cap is formed in situ upon withdrawal. The disclosure further relates to electrode assemblies, including electrolysis electrodes, produced by such methods.

## BACKGROUND OF THE INVENTION

[0004] Carbon and graphite are widely used as electrode materials in electrolysis, electrochemical synthesis, batteries, arc devices, resistance heating, and electrical machinery, owing to their electrical conductivity, chemical inertness, low cost, and high temperature capability. A persistent practical difficulty, however, is the attachment of a metallic conductor to

a carbon body with low and stable contact resistance. Molten soft solders and most common engineering metals, including lead, tin, copper, silver, and gold, do not wet graphite; in non-reactive metal/carbon systems, only weak van der Waals dispersion forces act between the metal and carbon atoms, and contact angles on the order of 120 degrees are observed. Conventional soldering of a wire directly to a graphite surface is therefore not possible without special measures.

[0005] The prior art has addressed this difficulty in several ways, each with disadvantages. A first family of solutions relies on pressure contacts: clamps, screw threads, spring clips, press-fitted metal caps, and bolted lugs. For example, dry cell batteries historically employed a brass cap driven onto the projecting end of the carbon rod with a tight fit, to which an external conductor could then be soldered (see, e.g., U.S. Patent No. 1,224,376). Arc lamp carbons and furnace electrodes have employed threaded connections and clamping holders (see, e.g., U.S. Patent Nos. 4,006,380 and 4,397,026). Pressure contacts require fabricated hardware sized to the carbon body, may loosen with vibration or thermal cycling, and are prone to a self-reinforcing degradation mode in which localized heating at a small contact area promotes oxidation, which raises contact resistance, which further increases heating.

[0006] A second family of solutions deposits an intermediate metal layer on the carbon prior to soldering. Carbon arc electrodes are routinely supplied with an electroplated copper cladding; carbon brushes have been provided with galvanic metal platings to which leads are then soldered (see, e.g., U.S. Patent No. 5,263,562, discussing DE-OS 34 05 674); and carbon and graphite fibers, cloths, and films have been provided with low-resistance terminals by first electroplating the carbon edges with a metal such as copper or silver and thereafter soldering to the plated metal, for example by dipping the plated edges into a molten solder bath (see, e.g., U.S. Patent No. 4,631,118). Electroplating and electroless deposition require plating baths, surface activation, and process control that are poorly suited to field work, small shops, and one-off electrode fabrication.

[0007] A third family of solutions employs reactive metallurgy. U.S. Patent No. 3,119,171 discloses forming low-resistance contacts on graphite by first causing indium to penetrate the graphite and thereafter dipping the graphite into molten lead at about 400 °C, whereby a lead-indium alloy forms at the surface, to which a connection is then soldered. Active solder alloys

containing titanium, cerium, or other carbide-forming additions (e.g., Sn-Ag-Ti and related compositions) can wet carbon directly, particularly with ultrasonic agitation, and brazing systems employing carbide-forming metals such as chromium, zirconium, niobium, tantalum, and hafnium have been used to join graphite arc electrodes to refractory metal contact spuds (see, e.g., U.S. Patent No. 4,109,125). These approaches require costly specialty alloys, indium, ultrasonic equipment, plasma spraying, or controlled-atmosphere furnaces, and the need for indium pre-impregnation and a high-temperature bath teaches away from forming a solderable termination by a brief, low-temperature dip of bare carbon.

[0008] A fourth family of solutions embeds metal hardware in the carbon. Carbon brush shunts are conventionally anchored by tamping conductive powder around a cable end inserted into a drilled and rifled hole (see, e.g., U.S. Patent Nos. 4,075,524 and 4,579,611). U.S. Patent No. 2,507,780 discloses attaching a conductor to a carbon brush by fitting a hollow metal rivet through the brush and dipping the assembly into molten silver solder at about 1300 °F for about two minutes; the solder takes hold of the rivet and of a fluxed conductor loop but falls away from the unfluxed carbon, and on cooling the rivet contracts to increase clamping pressure. Notably, this reference confirms that molten metal baths do not adhere appreciably to bare carbon under the conditions there described, and for that reason teaches that embedded metal hardware is required for a dip process to produce a termination, thereby teaching away from producing a termination by dipping bare carbon without such hardware.

[0009] A fifth family of solutions, employed at industrial scale in chlor-alkali electrolysis prior to the adoption of coated titanium anodes, cast the lower ends of consumable graphite anodes directly into a lead slab forming part of the cell base, the lead casting being protected from the electrolyte by concrete or bitumen (see, e.g., U.S. Patent Nos. 4,078,986 and 4,116,802, describing this as common practice). Such cast-in-lead connections demonstrate that a purely mechanical lead-to-graphite cast interface can carry very large currents reliably, but the known practice involved casting a massive stationary slab around fixed anodes and provided no individual, portable, solderable terminal on a rod end.

[0010] There remains a need for a method of providing a solderable metallic terminal on an end of a carbon or graphite body that requires no plating bath, no specialty active alloy, no embedded hardware, no ultrasonic or furnace equipment, and no machining of mating metal parts; that can

be performed in seconds with equipment no more elaborate than a heated pot of inexpensive metal; and that yields a terminal to which ordinary electrical solder joints can thereafter be made with a conventional soldering iron.

## **SUMMARY OF THE INVENTION**

[0011] The present invention provides a method of forming a solderable, mechanically self-retaining metal cap on an end portion of a carbon body, such as a graphite rod, by briefly immersing the end portion in a pool of molten metal, preferably a lead-based or lead-free solder alloy, maintained at a temperature only slightly above the liquidus temperature of the metal, and promptly withdrawing it. The invention deliberately exploits three physical phenomena that the prior art treated as obstacles or ignored.

[0012] First, because the molten metal does not wet carbon, the metal neither runs along nor is rejected cleanly from the immersed end when the bath is held at low superheat: instead, the chilling action of the carbon dominates. Second, the carbon body, having substantial thermal mass and high thermal conductivity relative to the thin layer of melt adjacent to it, extracts heat from the surrounding melt so rapidly that a shell of metal freezes in situ around the immersed end portion before the non-wetting melt can drain away during withdrawal. Within the operative low-superheat range, and for a given dwell time and carbon heat capacity, a lower bath superheat tends to increase the thickness of the shell formed per immersion. Third, upon cooling, the metal shell contracts onto the carbon end portion, primarily because the coefficient of thermal expansion of the capping metal (on the order of  $29 \times 10^{-6}/^{\circ}\text{C}$  for lead and lead alloys, and in every case greater than that of carbon for the tin-, zinc-, and bismuth-based alloys used herein) greatly exceeds the coefficient of thermal expansion of graphite (typically about 2 to  $8 \times 10^{-6}/^{\circ}\text{C}$ , and in every case less than that of the capping metal), so the metal contracts more than the carbon over the cooling interval, while volumetric solidification shrinkage contributes additionally. The result is a shrink-fit cap that grips the carbon with substantial radial pressure, mechanically conforms to and interlocks with macroscopic surface irregularities of the carbon, and, in porous carbon forms, additionally infiltrates the open pore or fiber network, and presents an external metallic surface to which electrical conductors may be soldered using conventional solders, fluxes, and irons. It is not essential to the invention whether the molten metal is strictly non-wetting or exhibits slight or local wetting of the carbon; in either case the cap is retained

substantially by mechanical means, namely shrink-fit pressure and macroscopic interlock, rather than by chemical bonding or carbide formation.

[0013] In preferred embodiments the bath is maintained at a superheat of no more than about 50 °C above the liquidus, more preferably no more than about 25 °C, and most preferably between about 5 °C and about 15 °C; the dwell time of the immersion is, most generally, simply terminated before heat absorbed by the carbon body and surrounding pool remelts the freshly solidified shell, a self-indicating condition readily observed in practice; in typical embodiments the dwell is less than about five seconds, preferably less than about two seconds, and in many cases less than about one second; and the end portion of the carbon body is provided with one or more retention features, such as a circumferential groove, knurling, a reduced-diameter neck, a transverse hole, or a dovetail or undercut profile, into which the freezing metal flows so that the solidified cap is positively interlocked against axial removal in addition to being shrink-fitted. A discrete retention feature is preferred but not required, because the freezing metal also interlocks with the macroscopic surface texture inherent to a machined, filed, or abraded carbon surface. In some embodiments a transverse hole is formed through the end portion so that the freezing metal fills the hole and solidifies as a pin integral with the cap and extending through the carbon body, locking the cap against both axial removal and rotation. In some embodiments an electrical conductor is held against the end portion during immersion and is thereby cast into and embedded in the cap, joining the conductor to the cap without a separate soldering step. The carbon body may optionally be rotated about its longitudinal axis during immersion, withdrawal, or both, to promote a circumferentially uniform, concentric cap and to shed excess unsolidified metal. The immersion and withdrawal may be repeated one or more times to build cap thickness, each successive dip freezing an additional layer onto the previously formed cap, to which molten metal of like composition readily fuses.

[0014] The invention further provides electrode assemblies comprising a carbon body bearing such an in-situ dip-cast cap and an electrical conductor electrically connected to the cap, optionally with the cap and connection overcoated by a sealing or insulating material for protection in corrosive environments such as electrolysis cells. The capping metal may be a lead-based alloy or, equally, a lead-free metal, including tin, tin-copper, tin-silver-copper, tin-bismuth, zinc and zinc-aluminum alloys, and low-melting fusible bismuth-tin-indium alloys, the last being useful for thermally sensitive carbon forms; lead-free capping metals are preferred where the

finished electrode must satisfy restrictions on lead content or contact potable water, foodstuffs, or biological media. Because the method requires only a small melting pot, an inexpensive metal such as common plumber's solder, wheel-weight alloy, lead-antimony alloy, or lead-free solder, and a few seconds of operator time per electrode, it is particularly suited to laboratory, pilot-plant, field, and small-shop fabrication of electrolysis electrodes, ion-exchange-membrane cell current collectors, redox-flow-battery and fuel-cell carbon-felt terminals, sacrificial anodes, carbon-arc devices, resistance heaters, instrumentation contacts on graphite, and current-collecting terminals on porous carbon felt, cloth, and foam electrodes.

### **BRIEF DESCRIPTION OF THE DRAWINGS**

[0015] FIG. 1 is a side elevation view of an end portion of a graphite rod prepared with an exemplary circumferential retention groove in accordance with an embodiment of the invention.

[0016] FIG. 2 is a schematic sectional view showing the end portion of the rod of FIG. 1 immersed in a pool of molten lead alloy maintained at low superheat in a heated crucible, with a temperature sensor monitoring bath superheat.

[0017] FIG. 3 is a side elevation view of the rod immediately after withdrawal, showing the solidified metal cap frozen in situ on the end portion.

[0018] FIG. 4 is an enlarged sectional view of the cap-to-carbon interface of FIG. 3, showing conformance of the cap to macroscopic surface irregularities of the carbon, mechanical interlock regions, occupation of the retention feature, and shrink-fit contact pressure.

[0019] FIG. 5 is a side elevation view of a completed electrode assembly in which an electrical conductor has been soldered to the cap and the joint has been overcoated with a protective sealing material.

[0020] FIG. 6 is a flow diagram of a method according to an embodiment of the invention.

[0021] FIG. 7 is a side elevation view of an embodiment in which the carbon body is a sheet of carbon felt having a gathered tab, the tab bearing an in-situ dip-cast cap with the capping metal infiltrating the fiber network, and a conductor soldered to the cap.

[0022] FIG. 8 is an enlarged sectional view of an embodiment in which a transverse hole through the end portion is filled by the capping metal to form a pin integral with the cap and extending through the carbon body.

[0023] FIG. 9 is a side elevation view of an embodiment in which an electrical conductor is cast into and embedded in the cap during dipping, joining the conductor to the cap without a separate soldering operation.

## **DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS**

[0024] Reference will now be made to embodiments illustrated in the drawings. The embodiments are exemplary; the invention is defined by the claims and is not limited to the particular dimensions, alloys, temperatures, or geometries described.

[0025] Referring to FIG. 1, a carbon body 10 is shown as a cylindrical graphite rod, for example an extruded or isostatically molded graphite rod, an electric discharge machining (EDM) graphite blank, a gouging rod from which any copper cladding has been removed at the end to be capped, or a battery-grade carbon rod. The carbon body 10 has an end portion 12 intended to receive the cap. Diameters from about 2 mm to about 50 mm are contemplated, although the method is not limited to any particular diameter or to circular cross-sections; plates, bars, and blocks may likewise be capped along an edge or end region, and highly porous carbon forms, including carbon felt, carbon cloth, carbon paper, carbon foam, reticulated vitreous carbon, glassy carbon, pyrolytic graphite, flexible expanded-graphite foil, and carbon-fiber tow or yarn, may be capped along a margin, tab, or gathered edge, in which case the capping metal additionally infiltrates the open pore or fiber network to a depth determined by dwell time and superheat, substantially increasing both mechanical retention and electrical contact area. In the illustrated embodiment, the end portion 12 is provided with a retention feature 14, shown as a circumferential groove of generally rectangular or rounded profile, for example about 0.5 mm to about 3 mm deep and about 1 mm to about 5 mm wide, machined, filed, or abraded into the rod at a distance of about one-half to about two rod diameters from the tip. Alternative retention features include knurling, a reduced-diameter turned neck, one or more transverse through-holes or blind holes, a dovetail taper that widens toward the tip, threads, or simply coarse abrasion of the surface. A retention feature is preferred but not required; on rougher grades of carbon, shrink-fit pressure together with mechanical interlock at the macroscopic surface texture alone

provides useful retention, and on porous grades the additional infiltration of the open surface structure further increases retention. In some embodiments the carbon body is one whose open porosity has been impregnated or sealed, for example with a cured drying oil such as linseed or tung oil, a resin, a wax, pitch, or a like pore sealant, as is conventionally done to reduce the porosity and electrolyte penetration of graphite electrolysis electrodes; in such embodiments the surface of the end portion to be capped is left free of any metallic, plated, or fluxed layer, whether or not the carbon is impregnated within its pores, so that the capping metal solidifies directly against the carbon and interlocks with its macroscopic surface texture as described herein. Where the capped region is a porous current collector intended to be infiltrated by the capping metal, such as carbon felt or foam, that region is preferably left unimpregnated so that infiltration is not impeded; and where the capping metal is melted at a temperature above the decomposition temperature of the impregnant, the impregnant is preferably removed from the surface to be capped, kept below its decomposition temperature, or replaced by a lower-melting capping metal, to avoid outgassing at the cap. For an impregnated or sealed carbon body, the cap is retained by shrink-fit and macroscopic interlock alone, the pore-infiltration contribution otherwise available on unimpregnated porous carbon being intentionally forgone.

[0026] The end portion 12 is preferably clean and dry. Graphite is hygroscopic in its open porosity, and adsorbed moisture or machining fluids can flash to vapor on immersion, producing spatter and voids in the cap. Accordingly, in preferred embodiments the end portion 12 is preheated before immersion, for example to between about 105 °C and about 200 °C for a time sufficient to drive off moisture, conveniently by holding the rod above the melt pool or in a drying oven. Preheating is optional and is not a required step of the method; carbon that is already in a dry condition, or a low-porosity or non-porous carbon form, may be immersed without any preheating or drying step, in which case the full chilling capacity of the cold carbon is retained and tends to increase the thickness of the frozen shell. Preheating moderates thermal shock but, by reducing the chilling capacity of the carbon, somewhat decreases the shell thickness obtainable per dip; the practitioner may trade preheat temperature against dip count. Loose dust is removed by wiping or air blast. No flux is applied to the carbon, and none is required, because the process does not rely on wetting. Optionally, and as an alternative to preheating, the end portion is actively chilled below ambient temperature before immersion. Preheating and pre-chilling are mutually exclusive conditioning options for a given immersion,

and either may be omitted. Pre-chilling increases the temperature difference between the carbon and the melt, and therefore the heat the carbon extracts, so that the chilled end portion extracts more heat than the same end portion at ambient temperature and a thicker shell solidifies per immersion, permitting a usable cap to be formed in fewer dips, or in a single dip on a thin, low-thermal-mass form such as felt, cloth, or paper. For most purposes the end portion is chilled to between about 0 °C and about minus 80 °C, conveniently by refrigeration, a freezer, contact with solid carbon dioxide (about minus 78 °C), or a stream of chilled gas. Deeper chilling, for example with liquid nitrogen (about minus 196 °C), is reserved for thin, low-thermal-mass forms such as carbon felt or cloth, where it enables a single-dip cap; on dense or brittle carbon such deep chilling is generally avoided, because the large temperature excursion on immersion can fracture the carbon and, with the bath at low superheat, can freeze the melt non-uniformly and yield a less conformal cap. Pre-chilling is preferably applied to dense, low-porosity carbon, which holds little adsorbed water, rather than to hygroscopic open-porosity grades, and because a surface below ambient temperature condenses moisture or frost from humid air, which can flash to vapor on immersion, pre-chilling is preferably carried out in a dry or inert atmosphere or enclosure, with any frost removed and the chilled end portion immersed within a few seconds of removal.

[0027] Referring to FIG. 2, a melting vessel 20, such as a cast iron or steel pot heated electrically or by flame, contains a pool 22 of molten capping metal. The capping metal may be either a lead-based alloy or a lead-free metal, both of which are primary embodiments. A lead-based alloy means an alloy containing at least about 50 weight percent lead; exemplary lead-based alloys include tin-lead solder alloys such as 60Sn-40Pb (liquidus about 188 °C) and 63Sn-37Pb eutectic (about 183 °C), which, while tin-rich, behave equivalently in this process and are expressly within the scope of the term “solder alloy” as used herein; lead-tin alloys such as 95Pb-5Sn; lead-antimony alloys such as 94Pb-6Sb (liquidus about 285 °C), of the type conventionally used for plating anodes and castings; lead-tin-silver alloys; and commercially pure lead (melting point 327.5 °C). Lead-free capping metals, which are preferred wherever the finished electrode must meet restrictions on lead content or must contact potable water, foodstuffs, or biological media, include tin, tin-copper, tin-silver-copper (SAC) alloys, tin-antimony, tin-bismuth, bismuth-based fusible alloys, and zinc and zinc-aluminum alloys; zinc-aluminum alloys (near-eutectic liquidus about 382 °C) and near-pure zinc (melting point about

420 °C) yield harder caps at the cost of higher process temperature and more aggressive dross formation. Low-melting fusible alloys comprising bismuth with tin and/or indium, for example the 58Bi-42Sn eutectic (liquidus about 138 °C) or bismuth-tin-indium alloys such as the alloy known as Field's metal (about 62 °C), are a further lead-free embodiment having a liquidus below about 150 °C and are particularly useful for thermally sensitive carbon forms such as thin felt, carbon paper, and reticulated vitreous carbon, because the low pool temperature limits thermal shock; with such alloys the cap is retained principally by thermal-contraction interference and by interlock with and infiltration of the carbon, the coefficient of thermal expansion of the alloy exceeding that of the carbon. In each case the capping metal is selected to be free of carbide-forming elements, such as titanium, cerium, chromium, zirconium, niobium, tantalum, and hafnium, in an amount sufficient to form a carbide at an interface between the capping metal and the carbon body; the process relies on mechanical retention rather than on chemical bonding or wetting, and accordingly does not employ the active or carbide-forming additions used in reactive solders and brazes.

[0028] A significant aspect of the invention is the control of bath superheat, defined as the difference between the bath temperature and the liquidus temperature of the capping metal. The bath 22 is maintained, at the moment of immersion, at a low superheat: no more than about 50 °C, preferably no more than about 25 °C, and most preferably between about 5 °C and about 15 °C above the liquidus. At low superheat, the heat that must be extracted from the melt adjacent the carbon before freezing begins is minimized, so the chilling action of the carbon body freezes a thicker shell during a brief dwell. By contrast, at high superheat (for example, a bath at about 400 °C, roughly 70 °C above the melting point of lead and comparable to the lead bath temperature of U.S. Patent No. 3,119,171), a brief immersion of bare, non-wetting graphite, as distinguished from the indium-impregnated, wettable graphite of that reference, produces little or no retained shell, because the surrounding melt remains liquid and, being non-wetting, drains substantially completely from the carbon during withdrawal, as demonstrated by comparative Example 2 below. Bath temperature is conveniently monitored with a temperature sensor 23, such as a thermocouple or infrared thermometer; alternatively, the practitioner may operate near the lower limit by allowing a skin of solid metal to begin forming at the pool surface and breaking it immediately before the dip, which indicates the pool is at or barely above the liquidus.

[0029] Still referring to FIG. 2, the end portion 12 is immersed vertically or near-vertically into the pool 22 to a depth covering the intended cap length, including any retention feature 14, for a dwell time of less than about five seconds, preferably less than about two seconds, and in many embodiments between about 0.2 and about 1 second, and is then withdrawn smoothly. Optionally, the carbon body is rotated or spun about its longitudinal axis during the immersion, during the withdrawal, or both, for example at about 10 to about 300 revolutions per minute, by hand or by a simple motorized chuck. Rotation evens the thickness of the freezing shell about the circumference, counteracts gravity-driven asymmetry of any still-liquid film, centrifugally sheds excess unsolidified metal and the drip bead otherwise tending to form at the tip, and yields a smoother, more concentric, more dimensionally repeatable cap; continuing slow rotation for a few seconds after withdrawal, while the outer surface of the cap completes solidification, further improves symmetry. A pool-surface cover of charcoal, rosin, or oil may be used to reduce oxidation and dross on the bath; such cover acts on the pool and is not a flux applied to the carbon. The optimal dwell depends on rod diameter, preheat, and superheat: the dwell must be long enough for the melt to conform to the surface and the retention feature and for the chilled shell to form, but short enough that heat soaking back out of the carbon does not remelt the shell. For a 10 mm diameter room-temperature graphite rod in a 95Pb-5Sn bath at about 10 °C superheat, a dwell of about one-half to one second produces a continuous shell of about 0.5 mm to about 2 mm wall thickness. Excessive dwell is self-indicating: the shell remelts and the rod emerges nearly bare, since the non-wetting melt drains away. The process is therefore conveniently self-limiting and tolerant of unskilled operation, converging with at most a few trial dips.

[0030] Referring to FIG. 3, upon withdrawal the end portion 12 carries a solidified cap 24 of the capping metal, frozen in situ. The cap 24 conforms to the tip and side surfaces of the end portion and fills the retention feature 14. Referring to FIG. 4, at the interface the cap mechanically conforms to and interlocks with macroscopic surface irregularities of the carbon surface, including machining marks, filing or abrasion scratches, grain pull-out, dimensional waviness, and any engineered retention feature, the solidified metal occupying these irregularities at interlock regions 25; no metallurgical or chemical bond to the carbon is formed or required, the capping metal being free of carbide-forming elements in an amount sufficient to form a carbide at an interface between the capping metal and the carbon body, so that no carbide

forms at that interface. Whether or not slight or local wetting of the carbon occurs, retention is substantially mechanical. Where the carbon body is a fibrous or open-cell form such as felt, cloth, or foam, the capping metal additionally infiltrates the open pore or fiber network through a substantial thickness of the capped margin, the solidified metal enveloping individual fibers or struts. As the cap cools from the solidification temperature to ambient, the greater thermal contraction of the capping metal relative to the graphite, arising from the mismatch in coefficients of thermal expansion, places the cap in circumferential tension and the interface in radial compression, producing a shrink fit; this thermal-contraction interference is the principal retention mechanism and operates even for capping metals, such as bismuth-bearing fusible alloys, that exhibit little or no volumetric shrinkage on solidification, and in porous carbon forms it is supplemented by infiltration of and interlock with the open structure. The combination of shrink-fit pressure and macroscopic mechanical interlock at the surface irregularities and within any retention feature 14 retains the cap against axial pull, torsion, and vibration, and establishes distributed, intimate, low-resistance electrical contact over substantially the entire capped area, in contrast to the small contact spots characteristic of clamped connections.

[0031] If a thicker cap is desired, for example to carry higher current, to provide material for shaping, or to permit drilling and tapping, the immersion and withdrawal are repeated. On the second and subsequent dips, the bath metal contacts the solidified metal of the existing cap rather than bare carbon; because metal wets like metal, each successive dip fuses metallurgically to the prior shell while the carbon core again limits remelting, so the cap grows by increments of roughly the original shell thickness. Three to six dips with a few seconds of cooling between dips readily produce caps of 3 mm to 10 mm wall thickness. The cap may alternatively or additionally be built up or shaped after dipping by conventional means, including ladling, soldering-iron deposition, filing, turning, or dipping the end into a shaped mold cavity to cast a terminal feature such as a lug, boss, or threaded boss.

[0032] Referring to FIG. 8, in an embodiment a transverse hole 50 is formed, for example drilled, through the end portion 12 before immersion, at a location to be covered by the cap. During immersion the molten capping metal fills the transverse hole 50, and upon solidification the metal within the hole forms a pin 52 that is integral and continuous with the surrounding cap 24 and extends through the carbon body 10. The pin 52 mechanically keys the cap to the carbon, locking it against both axial withdrawal and rotation, and is formed in the same single dip that

forms the cap, without any separate fastener. One or more such transverse holes, blind holes, or cross-drillings may be used. In a related embodiment, a metal insert or terminal, such as a threaded insert, stud, ring lug, or tab, is brought into contact with the cap while the cap is still molten, so that the insert becomes embedded in and electrically joined to the cap upon solidification.

[0033] Referring to FIG. 5, an electrical conductor 26, such as a copper wire, braid, or lug, is joined to the cap 24 by a solder joint 28 using conventional soldering practice: the cap surface is brightened by scraping or abrasion if oxidized, rosin or acid flux appropriate to the solder is applied, and a tin-lead or lead-free solder is melted against the cap with an iron or torch at modest temperature. Because the cap 24 is itself a solder-compatible metal of substantial thickness backed by the heat-sinking carbon, the joint is made quickly without disturbing the cap. Mechanical alternatives are also enabled by the cap: the conductor may be wrapped and sweated, crimped within a sleeve swaged over the cap, captured under a screw driven into a drilled and tapped hole in a thick cap, or clamped, the cap in each case serving as the durable metallic terminal that bare carbon cannot provide.

[0034] Referring to FIG. 9, in a further embodiment the separate soldering operation is eliminated by casting the conductor 26 directly into the cap 24. An end of the conductor 26 is positioned against, alongside, or wrapped around the end portion 12 before immersion, optionally engaging the retention feature 14 or a transverse hole 50, and is held in place by a fixture or by its own spring. During the immersion and withdrawal, the freezing capping metal envelops and embeds the end of the conductor 26, so that on solidification the conductor is cast into and metallurgically continuous with the cap 24 and is electrically joined to it without a separate solder joint. The conductor is preferably of a metal, such as copper or a copper alloy, that is not melted at the bath temperature and to which the capping metal adheres; pre-tinning the conductor end improves the cast-in bond. In a related embodiment, an electrical current is passed through the conductor 26 and the pool 22 during the immersion, the conductor 26 serving as one electrical terminal and the pool 22, or an electrode immersed therein, serving as the other, so that current flows from the conductor through the molten capping metal. The current locally heats the conductor and the adjacent capping metal by resistive Joule heating and, depending on its polarity and magnitude, assists removal of surface oxide from the conductor, so that the capping metal wets and metallurgically bonds to the conductor even though the bath is held at low

superheat and would not otherwise readily wet an oxidized conductor at that temperature. The current is applied locally to the conductor and for a time short enough that the carbon body and the solidified shell are not appreciably heated and the shell is not remelted; the bare carbon surface, being non-wetting and not part of the heated path through the conductor, remains unwetted and mechanically retained as described. The current may be direct or alternating, continuous or pulsed, and is supplied by any suitable source; representative currents are on the order of amperes to tens of amperes at low voltage, selected together with the conductor gauge to heat the conductor without melting it. This current-assisted wetting strengthens the cast-in joint between the conductor and the cap while preserving the non-wetting, mechanically retained interface between the cap and the carbon.

[0035] For service in wet, corrosive, or electrolytic environments, the cap and connection are preferably positioned outside the liquid and overcoated with a protective sealing material 30, such as a sprayed or brushed coating of thinned polyvinyl chloride (PVC) or other paint or polymer solution, epoxy, bitumen, silicone, heat-shrink tubing with adhesive lining, or wax, in the manner long practiced for protecting the cast lead bases of graphite anodes. A fully encapsulating sealant additionally isolates a lead-bearing cap from the environment, preventing galvanic and chemical attack of the lead alloy in chloride or acidic media and preventing release of lead, so that even a lead-based cap may be used where bare lead would be objectionable; where the capped end cannot be kept fully out of the process environment, a lead-free capping alloy or a fully encapsulating sealant is preferred. At end of service, the cap metal may be melted off and recovered for re-use, consistent with closed-loop material handling. The completed assembly is an electrode suitable, without limitation, for electrolysis of aqueous or molten salt media, electrowinning and electrorefining, cathodic protection, plating, carbon-arc and resistance heating devices, and electrochemical instrumentation.

[0036] The capping method and the electrode assemblies described herein are useful across a range of electrochemical and electrical systems. Without limitation, the capped carbon body serves as: a current collector or electrode terminal in an ion-exchange-membrane electrolysis cell, including cells used for metal recovery, electrowinning, electrorefining, and acid regeneration; a current collector on a carbon-felt, carbon-cloth, or carbon-paper electrode of a redox flow battery; a current-collecting terminal or lead on a carbon electrode of a fuel cell or electrolyzer stack, located outside the active area; an electrode terminal in capacitive

deionization, supercapacitors, electrocoagulation, and electro-Fenton water treatment; a sacrificial anode or cathodic-protection connection; a terminal on carbon-arc, gouging, and resistance-heating electrodes; a grounding or earthing electrode connection; and a contact on graphite sensing, reference, and electrical-discharge-machining electrodes. In each case the cap provides the durable, low-resistance, solderable or cast-in terminal that bare carbon cannot.

[0037] Referring to FIG. 7, in a further embodiment the carbon body is a porous carbon body 40, shown as a sheet of carbon felt, of the type used as flow-through electrodes and current collectors in electrochemical cells. A margin of the sheet is gathered, folded, or compressed into a tab 42, optionally bound temporarily with wire. The tab 42 is dried and dipped according to the method described above; because the felt presents an open fiber network and very low thermal mass per unit area, superheat at the low end of the stated range and a brief dwell are preferred. The capping metal infiltrates the fiber network of the tab, and on withdrawal solidifies as a cap 24 enveloping the individual fibers, mechanically locking the cap to the tab and establishing electrical contact distributed over the very large internal fiber surface rather than at discrete pressure points. A conductor 26 is then soldered to the cap at solder joint 28, or cast into the cap as described with reference to FIG. 9, and the cap region is preferably sealed and kept out of the electrolyte. The same approach applies to carbon cloth, carbon paper, and carbon foam, a corner, edge, or lug region of which serves as the tab.

[0038] FIG. 6 summarizes a method according to an embodiment of the invention. At step 100, a carbon body having an end portion with a bare carbon surface is provided. At step 102, at least one retention feature is optionally formed in the end portion. At step 104, the end portion is optionally conditioned, either by preheating and drying to remove adsorbed moisture or, alternatively, by pre-chilling below ambient temperature, these being mutually exclusive options, the conditioning being omitted entirely in other embodiments. At step 106, a pool of molten capping metal is maintained at a low superheat, no more than about 50 °C above the liquidus temperature of the capping metal. At step 108, the end portion is immersed in the pool for a dwell time of less than about five seconds. At step 110, the end portion is withdrawn from the pool, whereupon a shell of the capping metal that has frozen in situ about the end portion is carried out of the pool and contracts onto the end portion upon cooling. At decision step 112, if a thicker cap is required, the immersing and withdrawing of steps 108 and 110 are repeated one or more times, each repetition fusing additional capping metal to the previously solidified shell; if

no further thickness is required, the method proceeds to step 114, at which an electrical conductor is soldered or cast to the cap and the cap and connection are optionally covered with a protective sealing material.

[0039] EXAMPLE 1. A 9.5 mm diameter EDM graphite rod was prepared with a 1.5 mm deep, 3 mm wide circumferential groove 10 mm from one end, dried at approximately 120 °C, and dipped to a depth of 15 mm for approximately 0.5 second into a 95Pb-5Sn pool held approximately 10 °C above its liquidus, then withdrawn. A continuous cap of approximately 1 mm wall thickness formed, filling the groove. Two further dips increased the wall to approximately 3 mm. A 14 AWG copper wire was soldered to the cap with 60Sn-40Pb solder and rosin flux in under five seconds of iron contact.

[0040] EXAMPLE 2 (comparative). The procedure of Example 1 repeated with the pool held approximately 80 °C above liquidus produced no retained cap; the melt drained from the rod on withdrawal, leaving only traces in the groove and surface pores. This comparison illustrates the criticality of low superheat to in-situ shell formation on bare carbon and distinguishes the present method from high-superheat dips of the prior art.

[0041] Definitions and conventions. As used herein, bath superheat (or superheat) is the amount, in degrees Celsius, by which the bath temperature exceeds the liquidus temperature of the capping metal, and low superheat means a superheat of no more than about 50 °C. In situ means that the cap is solidified directly upon the carbon end portion while that end portion is immersed in the pool, as distinguished from forming a cap separately and applying it. Shrink-fit means that the solidified cap, upon cooling, contracts onto the carbon and grips it under residual radial compression arising from solidification shrinkage and the greater thermal contraction of the capping metal relative to the carbon. Macroscopic surface irregularities means surface features visible to the unaided eye or at low magnification, such as machining marks, grooves, knurls, abrasion, grain pull-out, holes, and dimensional waviness, as distinguished from microscopic porosity. A bare carbon surface means a carbon or graphite surface that is free of any metallic, plated, metallized, or fluxed layer and free of any applied intermediate bonding layer before immersion; a carbon body whose open porosity has been impregnated or sealed with a non-metallic pore sealant, such as a cured drying oil, resin, wax, or pitch, still presents a bare carbon surface for purposes of this disclosure provided the surface to be capped is free of any

metallic, plated, or fluxed layer and free of any metal infiltrated into the porosity of the surface region to be capped, such that the capping metal solidifies against carbon rather than against an in-pore metal phase. A carbon body into whose surface porosity a metal, such as indium, has been infiltrated at the region to be capped does not present a bare carbon surface. The terms approximately and about accommodate ordinary measurement tolerance and process variation, and unless otherwise stated denote plus or minus 10 percent of the stated value or plus or minus 5 °C for temperatures, whichever is greater. Throughout this disclosure, carbon body includes bodies of graphite, amorphous carbon, carbon-graphite, metal-graphite of less than 50 weight percent metal, carbon-carbon composite, glassy carbon, pyrolytic graphite, and carbon in any physical form, including rods, plates, bars, blocks, tubes, felts, cloths, papers, and foams. As used herein, free of carbide-forming elements in an amount sufficient to form a carbide means that the capping metal contains less than about 0.1 weight percent in total of titanium, cerium, chromium, zirconium, niobium, tantalum, and hafnium. A working portion or working area of an electrode means the region of the electrode that contacts the process electrolyte or medium during operation, the cap preferably being located outside the working portion. Although embodiments have been described with particularity, modifications apparent to persons of ordinary skill in the art are within the scope of the appended claims.

## CLAIMS

What is claimed is:

1. A method of forming a solderable metallic terminal on a carbon body, the method comprising: providing a carbon body having an end portion with a bare carbon surface; providing a pool of molten capping metal maintained at a bath temperature exceeding the liquidus temperature of the capping metal by a superheat of no more than about 50 °C; immersing the end portion in the pool, whereby heat extraction by the carbon body solidifies a shell of the capping metal in situ about the end portion notwithstanding that the capping metal does not wet the bare carbon surface; and withdrawing the end portion from the pool after a dwell time insufficient for heat absorbed by the carbon body and the pool to remelt the shell, the shell contracting upon cooling onto the end portion to form a mechanically retained, electrically conductive, solderable cap on the carbon body.

2. The method of claim 1, wherein the superheat is no more than about 25 °C.

3. The method of claim 2, wherein the superheat is between about 5 °C and about 15 °C.

4. The method of claim 1, wherein the dwell time is less than about five seconds.

5. The method of claim 4, wherein the dwell time is less than about two seconds.

6. The method of claim 1, wherein the capping metal is a lead-based alloy comprising at least 50 weight percent lead.

7. The method of claim 6, wherein the lead-based alloy comprises lead and at least one of tin, antimony, and silver.

8. The method of claim 1, wherein the capping metal is a solder alloy selected from tin-lead alloys, tin-copper alloys, tin-silver-copper alloys, tin-bismuth alloys, and bismuth-based alloys.

9. The method of claim 1, wherein the capping metal is a zinc-based alloy.

10. The method of claim 1, wherein the capping metal is lead-free.

11. The method of claim 1, wherein the capping metal is a fusible alloy comprising bismuth and at least one of tin and indium and having a liquidus temperature below about 150 °C, and the carbon body is a porous carbon body.

12. The method of claim 1, further comprising, before immersing, forming at least one retention feature in the end portion, the retention feature selected from a circumferential groove, a knurled region, a reduced-diameter neck, a transverse hole, threads, and an undercut, and wherein the shell solidifies within the retention feature such that the cap is positively interlocked against axial removal.

13. The method of claim 1, further comprising, before immersing, forming a transverse hole through the end portion, wherein the capping metal fills the transverse hole during the immersing and solidifies therein as a pin integral with the cap and extending through the carbon body, the pin retaining the cap against axial removal and rotation.

14. The method of claim 1, further comprising, before immersing, heating the end portion to a temperature between about 105 °C and about 200 °C for a time sufficient to remove adsorbed moisture from the carbon body.

15. The method of claim 1, further comprising, before immersing, chilling the end portion to a temperature below ambient temperature, whereby the chilled end portion extracts more heat from the molten capping metal than the same end portion at ambient temperature and a thicker shell of the capping metal solidifies per immersion.

16. The method of claim 1, further comprising repeating the immersing and withdrawing at least once, wherein on each repetition molten capping metal fuses to a previously solidified shell to increase a thickness of the cap.

17. The method of claim 1, wherein the carbon body is a graphite rod and the end portion has a diameter between about 2 mm and about 50 mm.

18. The method of claim 1, wherein no flux is applied to the bare carbon surface and no metallic layer is deposited on the bare carbon surface before the immersing.

19. The method of claim 1, further comprising rotating the carbon body about a longitudinal axis of the end portion during at least one of the immersing, the withdrawing, and a period following the withdrawing during which the shell completes solidification, whereby the cap is rendered more uniform in circumferential thickness.

20. The method of claim 1, wherein the carbon body comprises carbon felt, carbon cloth, carbon paper, or carbon foam, and wherein the capping metal infiltrates an open pore or fiber

network of the end portion during the immersing, the solidified shell enveloping fibers or struts of the carbon body.

21. The method of claim 1, further comprising soldering an electrical conductor to the cap with a solder having a liquidus temperature lower than the solidus temperature of the capping metal.

22. The method of claim 21, further comprising covering the cap and the soldered conductor with a protective sealing material.

23. The method of claim 1, further comprising positioning an electrical conductor against the end portion before the immersing, whereby the electrical conductor is cast into and embedded in the cap during the immersing and the withdrawing and is electrically joined to the cap without a separate soldering operation.

24. The method of claim 1, further comprising bringing a metal insert into contact with the cap while the cap is molten, whereby the insert is embedded in and electrically joined to the cap upon solidification.

25. The method of claim 1, wherein the carbon body is impregnated or sealed within its open porosity with a non-metallic pore sealant, and the bare carbon surface of the end portion is free of any metallic, plated, or fluxed layer.

26. The method of claim 23, further comprising passing an electrical current through the electrical conductor and the pool during the immersing, the conductor serving as one electrical terminal and the pool, or an electrode immersed in the pool, serving as another, whereby the conductor is locally heated by resistive Joule heating and the capping metal wets and metallurgically bonds to the conductor while the bare carbon surface remains non-wetting, the current being applied for a time insufficient to remelt the shell.

27. An electrode assembly comprising: a carbon body having an end portion; a metal cap comprising a capping metal solidified in situ on a bare carbon surface of the end portion and shrink-fitted thereto, the capping metal being non-wetting with respect to carbon and free of carbide-forming elements in an amount sufficient to form a carbide at an interface between the capping metal and the carbon body, the cap mechanically conforming to and filling macroscopic surface irregularities of the bare carbon surface, in direct contact with the bare carbon surface

without an intervening adhesive, bonding layer, plating, or flux, and retained on the end portion by thermal contraction of the solidified capping metal; and an electrical conductor electrically connected to the cap.

28. The electrode assembly of claim 27, wherein the electrical conductor is soldered to the cap.

29. The electrode assembly of claim 27, wherein the electrical conductor is cast into and embedded in the cap.

30. The electrode assembly of claim 27, wherein the end portion comprises a retention feature and the cap occupies the retention feature such that the cap is positively interlocked against axial removal.

31. The electrode assembly of claim 27, wherein the end portion comprises a transverse hole and the cap includes a pin integral with the cap and extending through the transverse hole, the pin locking the cap against axial removal and rotation.

32. The electrode assembly of claim 27, wherein the capping metal is a lead-based alloy comprising at least 50 weight percent lead, and the cap has a wall thickness of at least about 0.5 mm.

33. The electrode assembly of claim 27, wherein the capping metal is lead-free.

34. The electrode assembly of claim 27, further comprising a protective sealing material covering the cap and the electrical conductor.

35. The electrode assembly of claim 27, wherein the carbon body is a graphite electrolysis electrode and the cap is located on an end of the electrode remote from a working portion of the electrode.

36. The electrode assembly of claim 27, wherein the carbon body is a current collector or an electrode of an ion-exchange-membrane electrolysis cell.

37. The electrode assembly of claim 27, wherein the carbon body is a carbon-felt current collector of a redox flow battery, and the cap is located on a margin of the carbon felt outside a working area thereof.

38. The electrode assembly of claim 27, wherein the capping metal contains less than about 0.1 weight percent in total of titanium, cerium, chromium, zirconium, niobium, tantalum, and hafnium.

39. The electrode assembly of claim 27, wherein the carbon body is impregnated or sealed within its open porosity with a non-metallic pore sealant, and the bare carbon surface is free of any metallic, plated, or fluxed layer.

## **ABSTRACT OF THE DISCLOSURE**

A solderable metallic terminal is formed on a carbon or graphite body by briefly immersing an end portion of the body in a pool of molten metal, preferably a solder alloy, maintained at low superheat above its liquidus, and promptly withdrawing it. Because the molten metal does not wet carbon and the carbon body rapidly extracts heat from the adjacent melt, a metal shell freezes in situ around the end portion before the melt can drain away, and on cooling the shell shrink-fits onto the carbon, interlocking with macroscopic surface irregularities and optional retention features such as grooves, knurling, or a transverse hole that fills to form an integral pin. The resulting cap is a durable, low-resistance terminal to which a conductor is soldered, or into which a conductor is cast, without plating, active solders, embedded hardware, or flux on the carbon. Electrode assemblies and overcoatings are also disclosed.

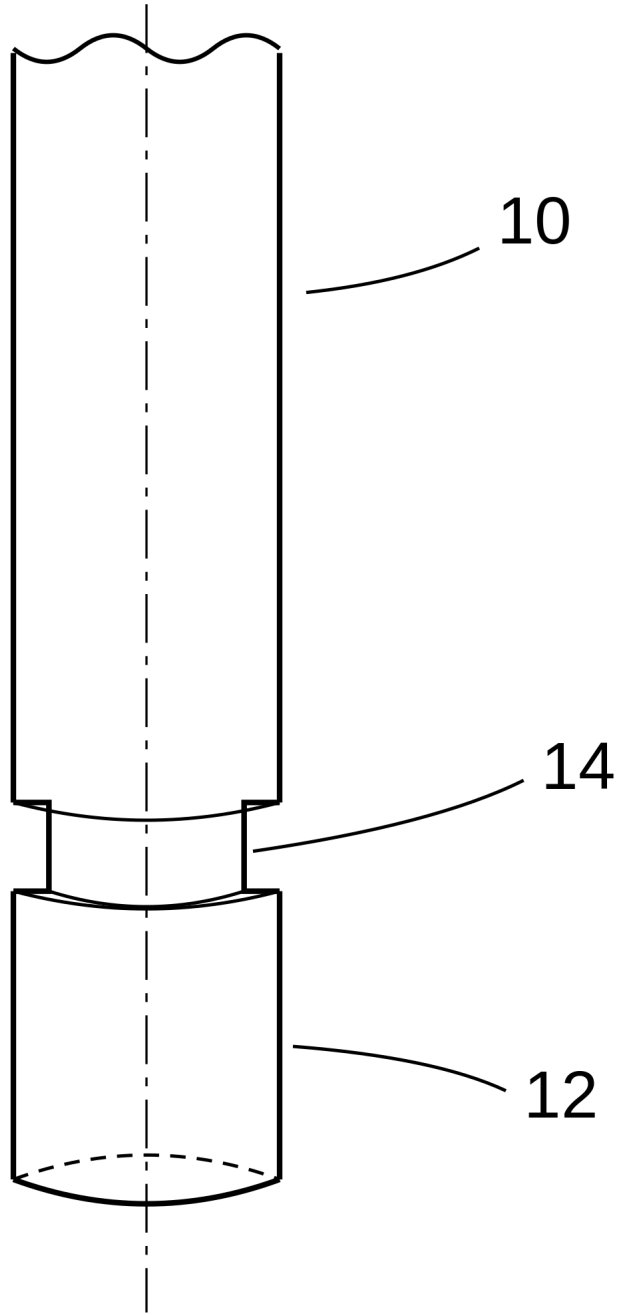


FIG. 1

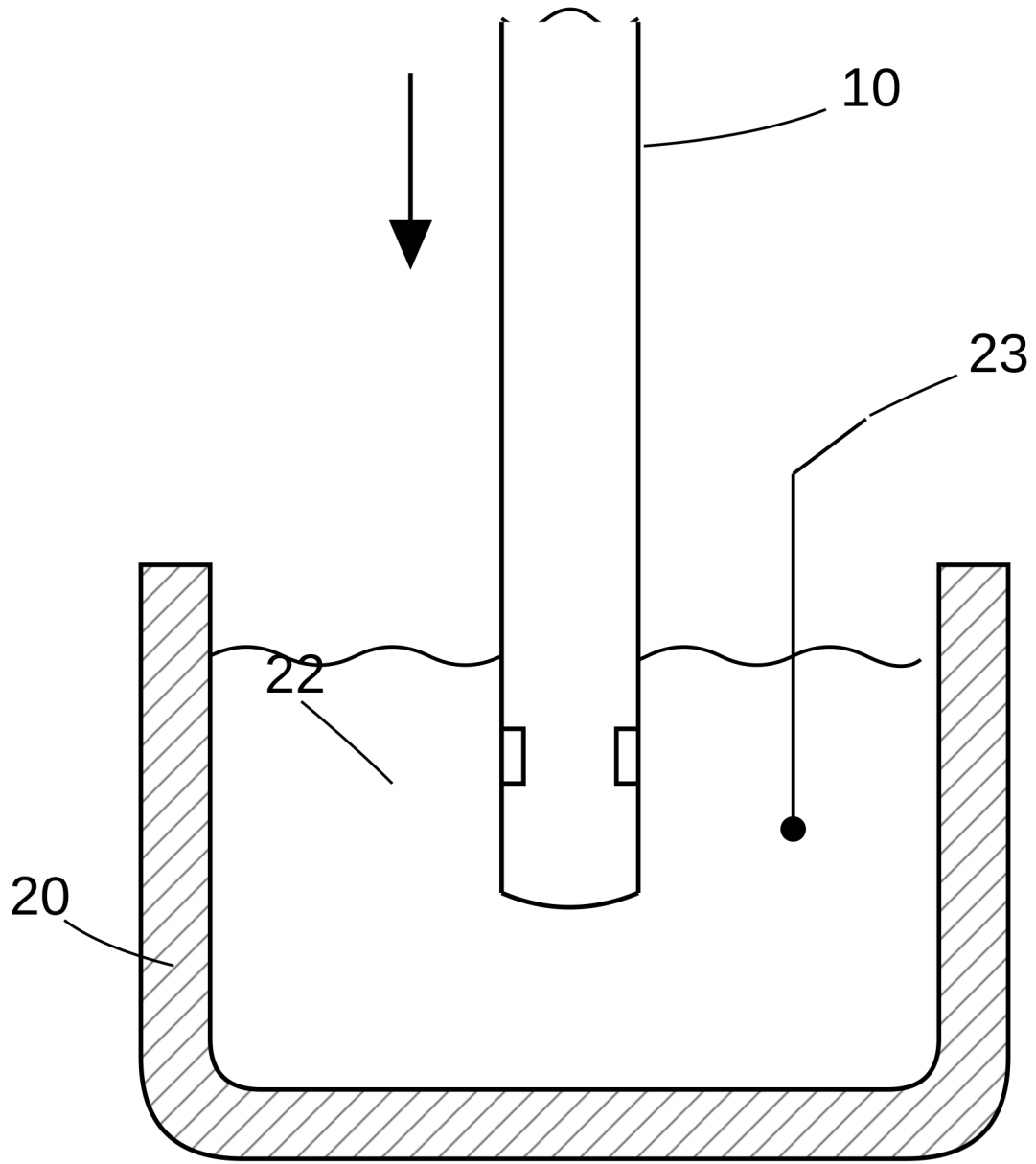


FIG. 2

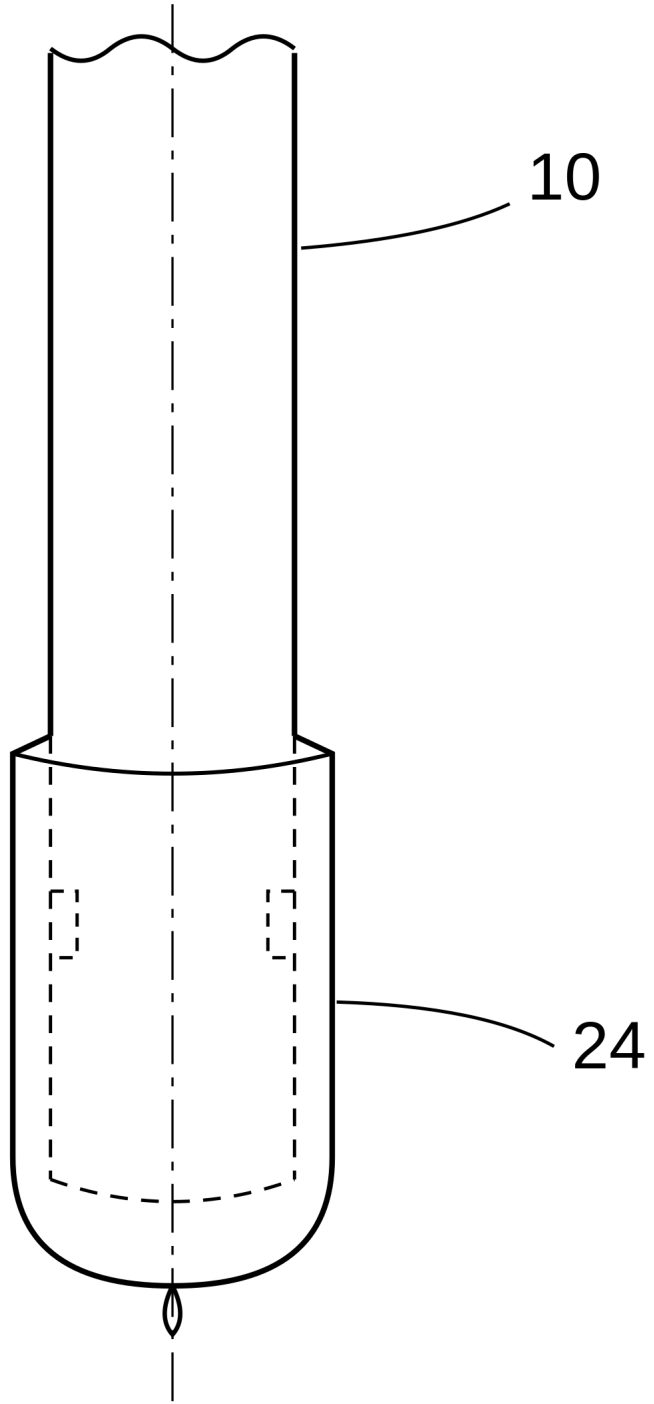


FIG. 3

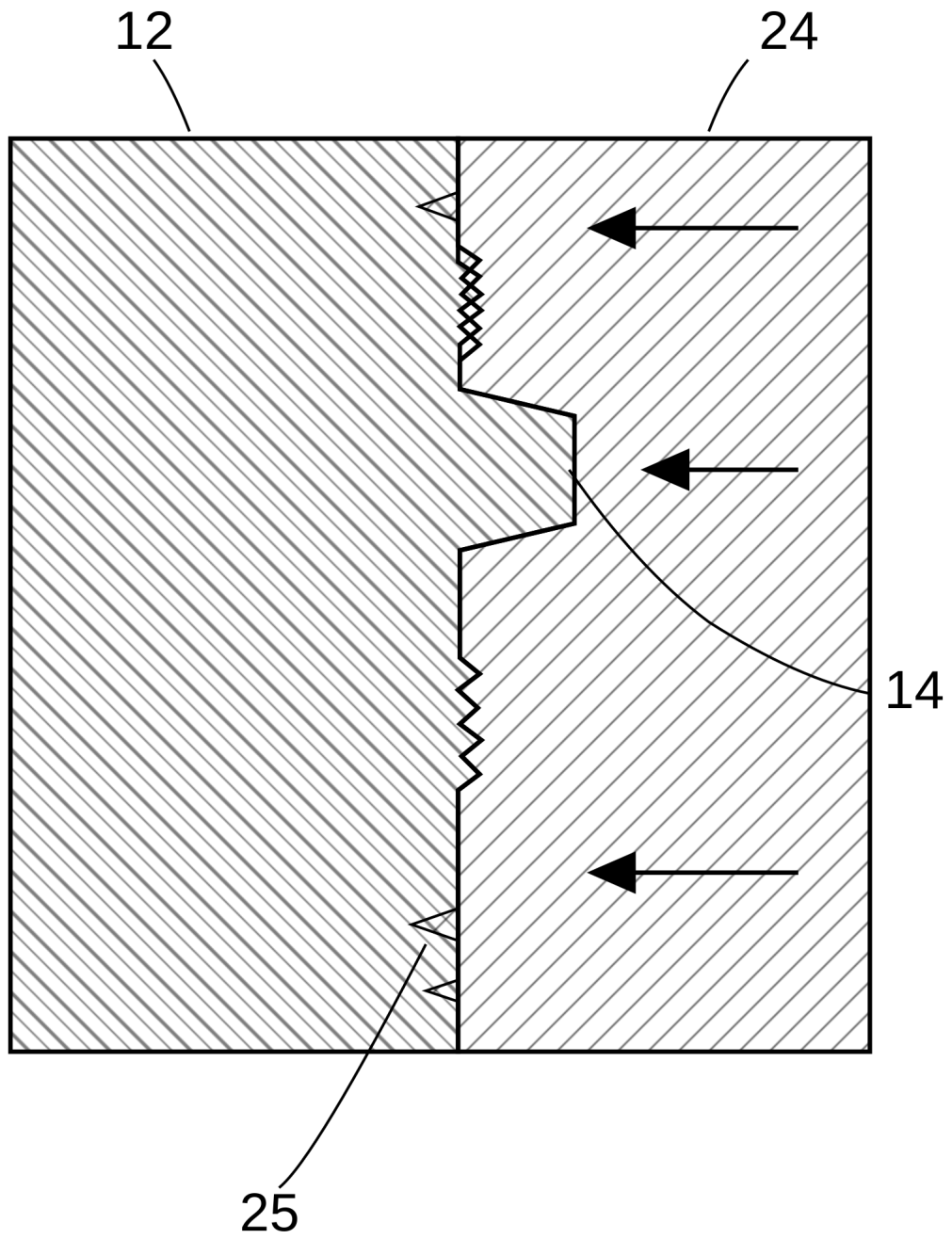


FIG. 4

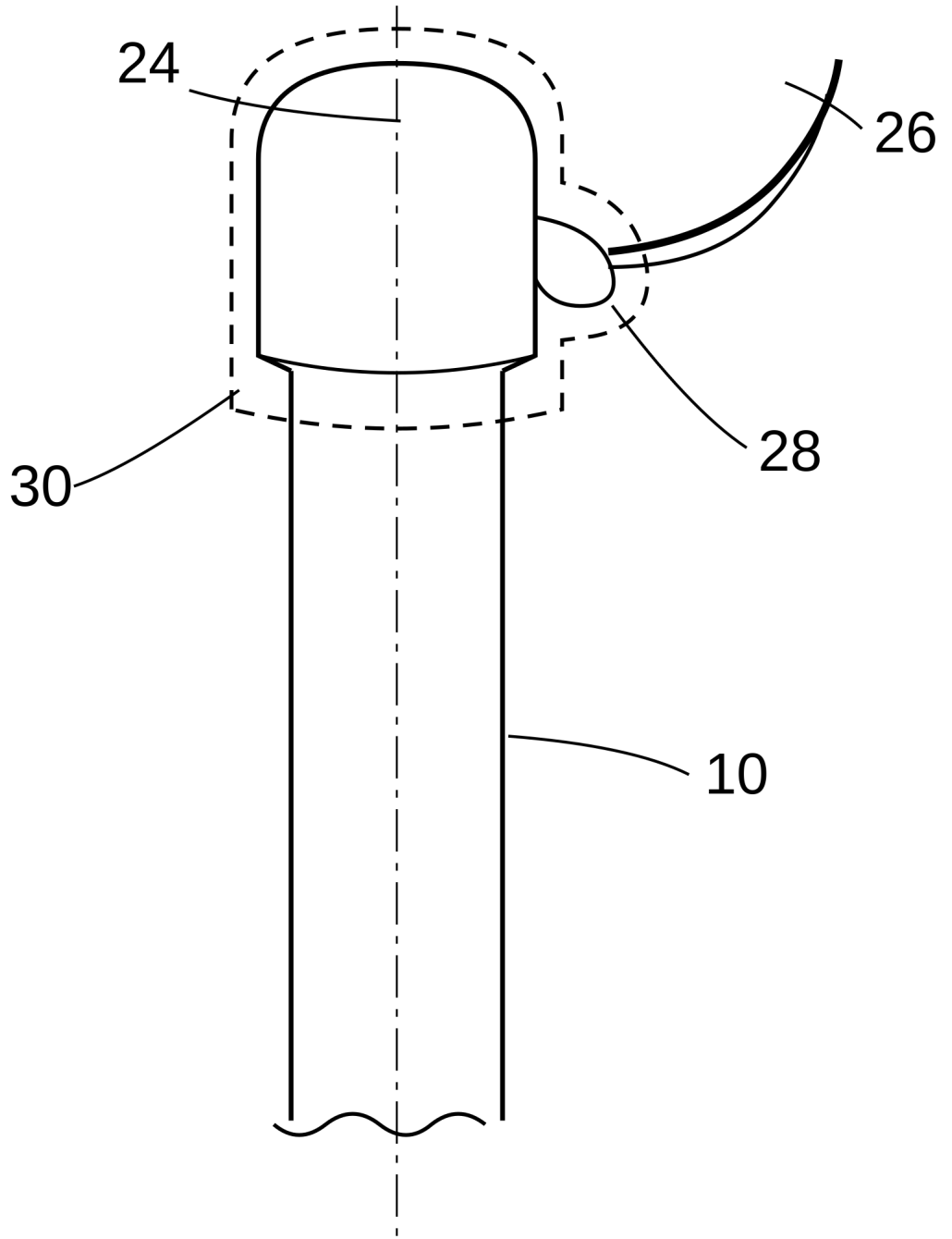


FIG. 5

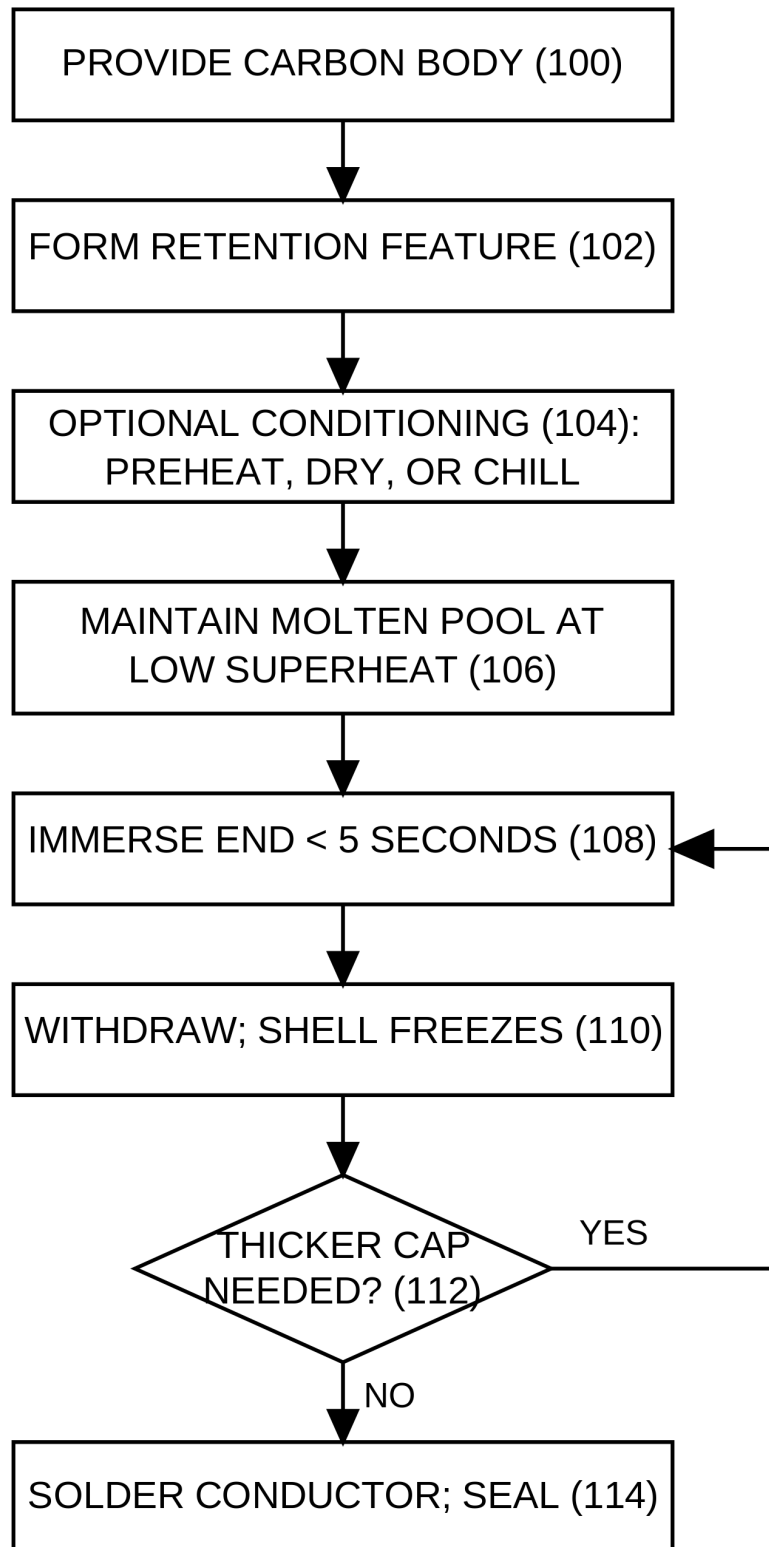


FIG. 6

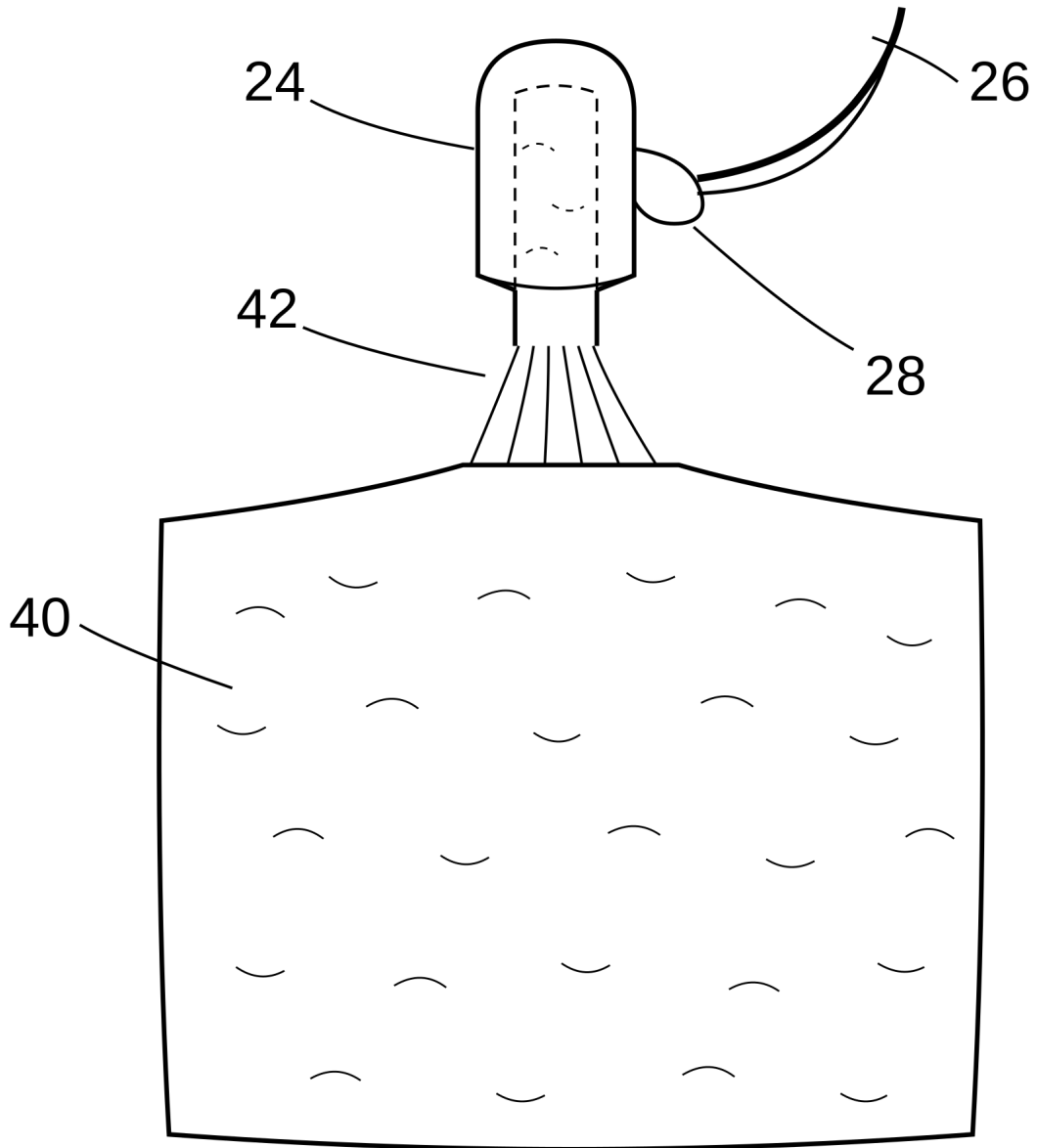


FIG. 7

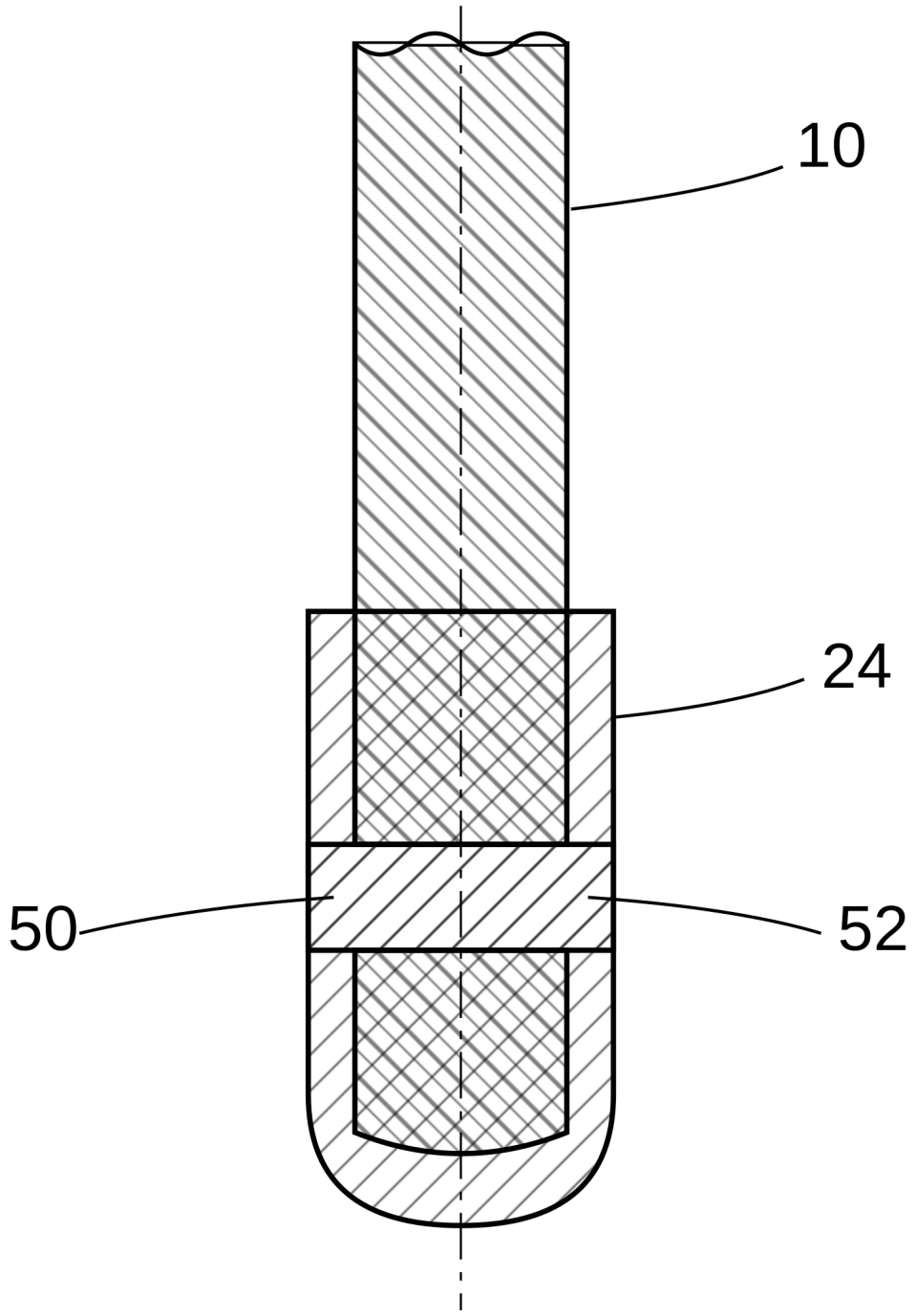


FIG. 8

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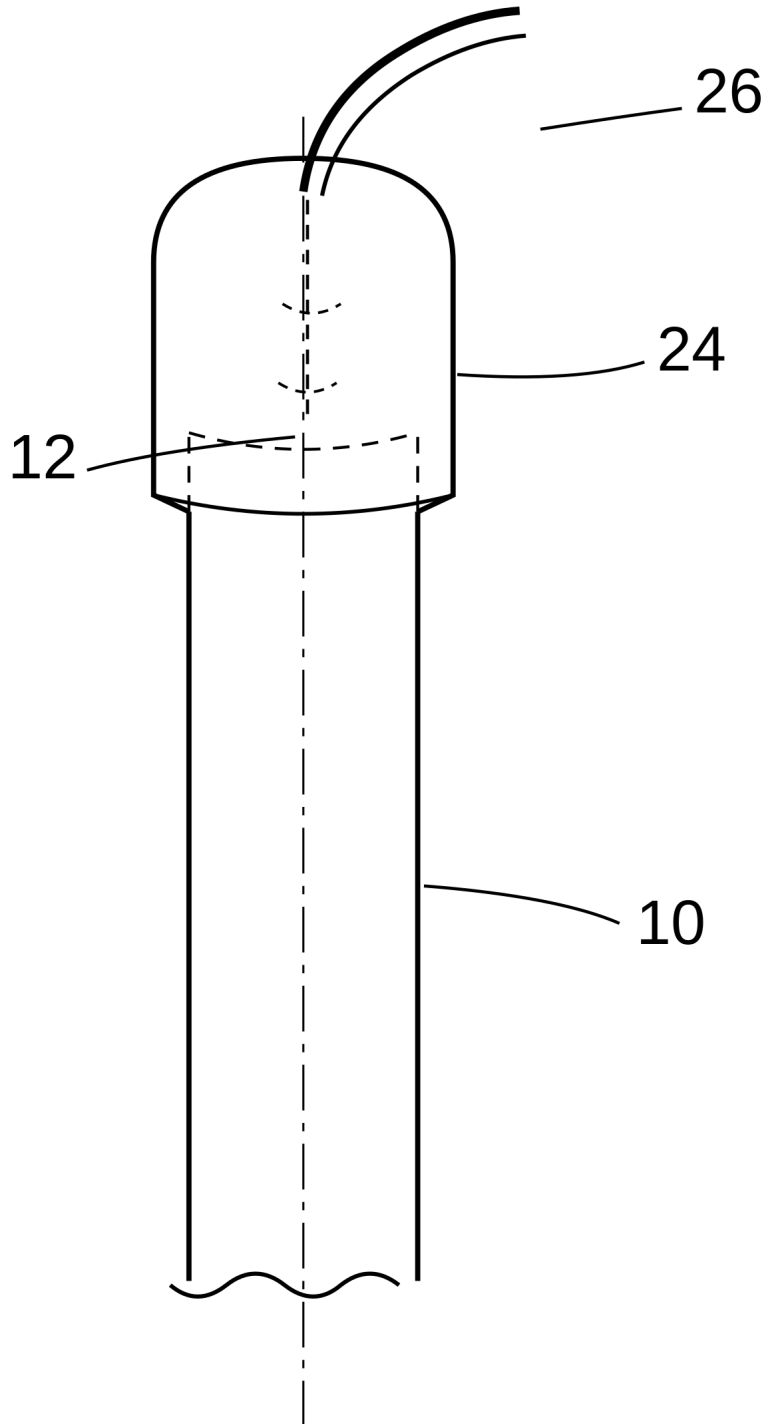


FIG. 9