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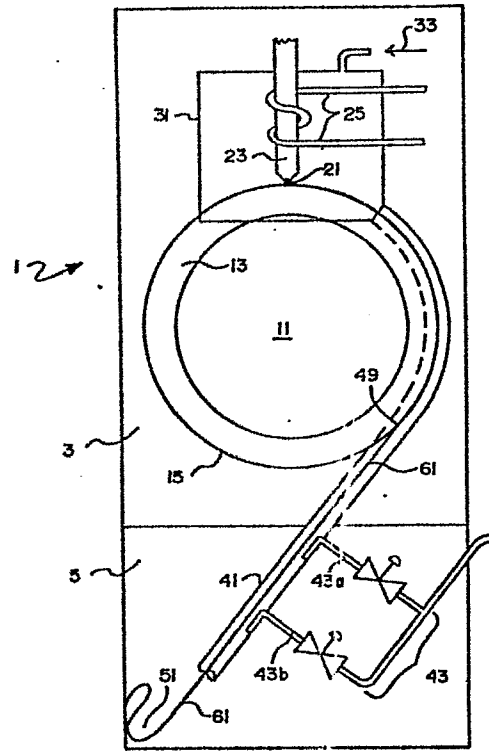
(54) **Method of forming disordered filamentary materials.**

(57) Disclosed are method and apparatus for quenching materials, where the quench duration is enhanced by providing a high speed gas jet (43) tensioning force beyond the intended point of ribbon take off.

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FIG. 1



METHOD OF FORMING DISORDERED FILAMENTARY MATERIALS

FIELD OF THE INVENTION

This invention relates to the synthesis of
disordered filamentary materials by rapidly quenching
5 a molten precursor material on a quench surface.

BACKGROUND OF THE INVENTION

Bulk disordered materials are useful because
10 of the properties derived from their disordered
structure. The disordered structure provides the
synthesist with the ability to tailor make the
electrical, thermal, magnetic, surface catalytic, bulk
catalytic, hydrogen storage, and ultimate properties
15 of the disordered material. Bulk disordered materials
e.g., alloys of transition metals, including
transition metals with semimetals are especially
useful as hydrogen storage materials, because of their
ability to reversibly form hydrides while retaining

Case 820

-2-

relatively constant physical, chemical and thermal properties, substantially independent of the number of cycles.

5 Bulk disordered materials, e.g., alloys of transition metals, rare earth metals, glass forming metals, and the like are also useful as permanent magnets. Exemplary magnetic materials include disordered, rapidly quenched alloys of iron, one or more rare earth metals, boron, and one or more further
10 non-metal or semimetal additives to enhance or stabilize particular properties.

In order to obtain the desired properties, it is necessary to rapidly quench liquid metals, thereby quenching in desired phases, morphologies, structures,
15 and compositions. In order to obtain disordered materials it is necessary to quench the molten material to the glass transition temperature at a rate substantially high enough to substantially avoid formation of the states obtained at low quench rates.
20 That is, the quench rate must be high enough to kinetically block the formation of ordered phases, ordered structures, and ordered morphologies, thereby inducing the formation of disordered phases, disordered structures, and disordered morphologies.

25 A preferred method of quenching is the discharge of the molten material onto a rapidly moving chill surface, whereby to form a thin filament of material thereon, where all regions of the thin filament are in a favorable thermally conductive geometry with respect to the chill surface. By this expedient, initial quench rates on the order of
30 10^5 - 10^7 °C per second are obtained, thereby providing the desired morphologies, structures, and phases herein contemplated.

35 One preferred method of attaining the aforementioned high quench rates is melt spinning in

which a jet of molten material is forced through a pressurized orifice onto a quench surface, where the surface moves at a velocity sufficient to provide a high quench rate, typically 1 to 50 meters per
5 second. In melt spinning, an extremely high quench rate is obtained for a brief period of time. However, the quench duration may be insufficient to quench the filament below the glass transition temperature. In
10 order to obtain disordered materials having a glass transition temperature far below the melting temperature, it is necessary to resort to other expedients to obtain a proper quench.

U.S. Patent 3,862,658 to Bedell, et al for
15 Extended Retention Of Melt Spun Ribbon On Quenching Wheel, discloses a method for the production of metal filament using a rotating quench wheel. A molten puddle is formed on the quench wheel, forming a solid filament on the quench wheel. The period of contact between the filament and the quench wheel is prolonged
20 by external means which act on the filament. The external means, which may be a gaseous stream imposing a downward, centripetal force on the filament, is applied over an elongated portion of the deposited filament, whereby to prevent separation of the
25 filament from the wheel. This partially overcomes the effects of centrifugal force. The gas stream further acts as an auxiliary chilling means.

More particularly, in Bedell, et al one or
30 more gas jets impinge inwardly against the forming metal filament stream on the wheel surface whereby to provide centripetal force to prevent the metal from departing from the wheel until the desired temperature is achieved. The gas may be impinged on the filament either directly i.e. from one gas jet, or through a
35 gas manifold.

Case 820

-4-

U.S. Patent 4,077,462 to Bedell, et al for Chill Roll Casting Of Continuous Filament, discloses that a stationary housing may surround the peripheral surface of the chill wheel in an arch. The arch
5 begins in the vicinity of the molten metal outlet of the crucible onto the chill wheel and terminates at a predetermined stripping, take off, or break away point where the solid filament is removed from the chill wheel. The stationary housing defines a gap between
10 the peripheral surface of the chill wheel and the interior of the housing. The housing includes means for providing a seal along the length of the housing between it and the chill wheel to prevent excessive escape of fluid. The gap between the chill wheel and
15 housing terminates in an outlet at the point for stripping solid filament from the chill wheel. Fluid is introduced into the gap defined by the housing and the chill wheel. The fluid passes through the gap in the direction of rotation of the chill wheel and is
20 angled to insure that the fluid passes in the same direction as the chill wheel. Bedell, et al discloses the introduction of air into the gap by means of air inlet ports located 50° and 80° from the point of metal inlet in the direction of rotation of the chill
25 wheel. The air is introduced at ambient temperature and a flow rate of 20 standard cubic feet per minute to each of the two fluid inlet ports, the velocity of fluid flow being twice the velocity of the chill wheel at its parameter.

30 In U.S. Patent 4,177,856 to Lieberman for Critical Gas Boundary Layer Reynolds Number For Enhanced Processing Of Wide Glassy Alloy Ribbon it is disclosed that a critical gas boundary layer Reynolds number is necessary at the metal-gas surface.
35 However, Lieberman does not extend the quench duration.

U.S. Patent 4,282,921 to Lieberman, et al for
Method For A Melt Puddle Control And Quench Rate
Improvements In Melt Spinning Of Metallic Ribbons,

describes a method for melt spinning metallic ribbon
5 where a melt stream is deposited onto the chill wheel
to form a molten alloy and a confluent gas is supplied
at a predetermined flow rate. The confluent gas is
coaxial with and encompasses the ejected metal stream,
bearing down on and surrounding the molten alloy
10 puddle as the solid metal strip is formed. Lieberman
provides hydrodynamic stability of the puddle, but
does not effect quench rate or duration.

The above methods of enhancing quench
properties do not materially enhance quench duration.

15

SUMMARY OF THE INVENTION

According to the invention herein
contemplated there is provided method and apparatus
20 for forming disordered material, e.g. filamentary
disordered material. As herein contemplated there is
provided a chill surface, a reservoir, and a gas jet
beyond the take off point, and, in a preferred
exemplification substantially tangential to the chill
25 surface with respect to the take off point. That is,
the gas jet is beyond the take off point. In a
preferred exemplification it is on a line extending
from the filament take-off point, tangential to the
chill surface.

30 According to the invention herein
contemplated there is also provided a method for
forming a disordered filamentary material. According
to the contemplated method a moving quench surface is
provided in proximity to a discharge orifice of a
35 vessel of molten material. The molten material is
forced from the vessel through the orifice onto the

-6-

moving chill surface. This causes a puddle of molten metal to form with a ribbon of quenched material forming on and carried by the chill surface means to a break off or take off point. A high velocity gas jet is introduced collinear to the ribbon, beyond the take off point. In a preferred exemplification the gas jet is on a line extending from and tangential to the take off point. The high velocity gas flow is introduced subsequent to the take off of the ribbon, and in contact with, and at a higher velocity than the ribbon, whereby to apply tension to the ribbon, keeping the ribbon on the quench surface to the take off point, in this way to increase the duration of thermal contact between the ribbon and the quench surface.

As herein used the term "disordered materials" means materials characterized by the substantial absence of long range order although they may have short range local order. Disordered materials include amorphous materials, microcrystalline materials, polycrystalline materials, and mixtures thereof. While the disordered materials may have zones, regions, and or inclusions of crystalline materials, this does not detract from their characteristics as disordered materials. Disordered materials may be characterized by thermodynamically unstable and/or metastable phases, regions, and morphologies.

As used herein, a "filament" is a slender metallic body having a quenched transversed dimension less than its length. Filaments, as used herein further include ribbons, sheets, wire and flakes as well as materials of irregular cross-section.

THE FIGURES

The invention may be understood by reference to the figures.

Figures 1 and 2 are partial cut away views of apparatus for practicing this invention including the
5 chill wheel, the crucible, gas blanket inlet means, gas jet inlet means, raceway, and the apron.

Figure 3 is a graphical representation of superconductive transition temperature versus film thickness and gas velocity for the contemplated melt
10 spinning system.

DETAILED DESCRIPTION OF THE INVENTION

Figures 1 and 2 illustrate two
15 exemplifications of the apparatus of the invention. The melt spinning system 1 herein contemplated is shown with an optional hot compartment 3 and an optional cold compartment 5. Within the hot compartment 3 is a quench surface means 11, for
20 example a chill wheel 13. The chill wheel 13 includes a high heat transfer surface 15 on the wheel 13. The chill surface means may further include means for maintaining high heat transfer surface of the chill wheel at a relatively constant temperature whereby to
25 maintain a high quench rate. Exemplary materials for formation of the high heat transfer surface include copper, molybdenum and the like. The quench surface is further characterized by the presence of means to provide relative motion thereto with respect to the
30 outlet 21 of a crucible 23.

The vessel of molten material, i.e. the crucible 23, is spaced, for example, vertically from the chill wheel and has discharge means 21 in proximity to the quench surface of the chill wheel

Case 820

-8-

11. The quench surface 15 moves with respect to the discharge means 21.

The crucible 23 shown in Figures 1 and 2 may be heated by radio frequency induction, with induction
5 coils 25 shown. Alternatively, the crucible may be heated with a resistance heater.

Optionally surrounding the chill wheel 11 and crucible 23 at the outlet point of the crucible 23 is a gas apron means 31. The gas apron means 31 is
10 supplied with a gas purge, for example a purge stream 33 of substantially nonreactive gas by nitrogen or carbon dioxide or a purge stream of an inert gas as helium, argon or the like, and is thusly argon.

The melt spinning system herein contemplated
15 further includes a raceway 41 extending from the apron 33 in the direction of rotation of the chill surface 15 to a filament collection area 51. In the exemplification shown in Figure 1, the raceway 41 is tangential to the chill surface 15 with respect to the
20 intended take off or break off point 49 of filament 61.

Positioned within the raceway 41 subsequent to the discharge point 21 of molten material and break off point 49 of ribbon are gas jet means 43, for
25 example, one or more gas jets 43a, 43b. The high velocity gas flow applies tension to the ribbon 61, preferably tangentially to the chill wheel 13 with respect to the break off point. The jet means 43 directs the gas flow in a direction substantially parallel to the flow of ribbon 61 after the break off
30 point 49 whereby to pull on and apply tension thereto, thereby keeping the ribbon on the wheel to the take off point 49.

As herein contemplated the invention further comprises a method of forming a disordered filamentary
35 material by providing quench surface means 11 and a vessel 23 of molten material. The vessel 23 has

Case 820

-9-

discharge effluent means 21 in proximity to the quench surface 11, the quench surface 11 moving rotationally with respect to the discharge means 21.

Molten material is discharged from the vessel 5 23 through the discharge effluent means 21 onto the rotational chill surface means 11 forming a puddle of molten metal thereon. A ribbon or filament 61 forms on the chill surface and is drawn along thereby to a break away on take off point 49. According to the 10 invention herein, the duration of thermal contact between the filament 61 and chill surface 11 can be increased by providing a high velocity gas jet 43 or gas jets 43a, 43b, subsequent to and beyond the intended break away or take off point, and preferably 15 tangential to the chill surface 11 with respect to the take off point 49. The gas jet 43 is provided subsequent to both the discharge 21 of the molten material and the intended break away 49 of ribbon, and in contact with, substantially parallel to, and at a 20 higher velocity than the ribbon 61 whereby to increase the duration of thermal contact between the ribbon 61 and the chill surface 11. The gas jet applies a tensioning force to the ribbon 61. The tension has a vector component opposing the centrifugal force acting 25 on the ribbon. This reduction in the resultant radial component of the forces acting on the ribbon 61 delays the time at which the ribbon 61 separates from the quench surface, assuring prolonged metal-to-metal heat transfer contact, and prolonging a high quench rate. 30 According to the method herein contemplated, gas jet means 43 may be from about 30 to 180 or more degrees subsequent the molten material discharge point 21, whereby to increase the arc and the contact time.

The gas jet is at a velocity of at least 1.5 35 times the velocity of the ribbon and preferably at a velocity of from about 2 to about 10 times the

-10-

velocity of the ribbon.

The gas used for the gas jet is substantially nonreactive with the ribbon. Nitrogen or an inert gas may be used. The preferred inert gas is argon
5 although helium, krypton, xenon or the like may be used.

The quench surface is a circular quench surface which may comprise circumferential heat sink means 13 on the rotating chill wheel.

10 The method of the invention may be utilized in any system in which the glass transition temperature is significantly below the melting temperature, and the system has sufficient tensile strength to allow quenching under tension. The method
15 of the invention is useful, for example, in the formation of hydrogen storage materials, exemplified by iron-magnesium alloys, iron-magnesium-aluminum alloys, and magnesium-carbon-copper-oxygen alloys.

The invention may be understood by reference
20 to the following example.

A number of samples of aluminum 80-silicon 20 were prepared by repeated melting in a tri-arc furnace. Thereafter individual portions were introduced into melt spinning apparatus having the
25 raceway herein contemplated. The samples were discharged from a crucible through a discharge orifice having a 0.5 mm diameter onto a 10 inch diameter, 1 inch width, chill wheel having a rotational velocity of about 2500 rpm. The chill wheel was configured
30 substantially as shown in Figure 1 having an apron of about 1.18 inches by about 3 inches and a raceway of about 20 inches long by about 3 inches in diameter. A discharge tube was present in the raceway about 3 inches beyond the ribbon break away point.

35 In one series of tests shown by solid circles in Figure 3, no high speed argon discharge was

Case 820

-11-

utilized, rather the chill wheel velocity was varied from about 2000 to about 3000 rpm whereby to show a superconductivity transition temperature as function of filament thickness and indirectly as a function of quench rate. It is noted that all transition temperatures were below 4.2°C , independent of thickness, showing insufficient total quench.

In a second series of tests, shown by open circles in Figure 3, the argon flow rate in the raceway was 40 cubic feet per minute (STP), and the discharge pressure was 20 psig. The wheel velocity was increased to decrease filament thickness. For a long quench duration, superconducting transition temperature is a function of quench duration and filament thickness, where the instantaneous quench rate is a function of filament thickness.

Thereafter three tests were carried out at increasing argon velocities through the tube, at a constant wheel velocity of about 2000 rpm to give a constant thickness of about 23 to 24 microns. The test results at 60, 80 and 100 cubic feet per hour (STP) from a 0.25 inch diameter discharge nozzle (43) into the raceway (41), are represented by the open triangles in Figure 3. The resulting filaments had a superconductivity transition temperature that was approximately linearly related to the jet gas flow rate independent of thickness. This shows improved total quench independent of thickness, and solely as a function of increased quench duration.

While the invention has been described with respect to certain exemplifications and embodiments thereof it is not intended to be limited thereby but solely by the claims appended hereto.

CLAIMS:

1. A method of forming a disordered
filamentary material (61) comprising the steps of:

(a.) providing circular quench surface means
(B);

5 (b.) providing a vessel of molten material
(32), said vessel having discharge means (21) in
proximity to the quench surface (15), said quench
surface means (13) rotating with respect to the
discharge means (21); and

10 (c.) discharging molten material from said
vessel through said discharge means (21) onto said
chill surface means (13) whereby to form a ribbon of
quenched material (61) thereon; characterized by
providing a jet (43) of a substantially non-reactive
15 gas subsequent to the discharge (21) of the molten
metal and the take off (41) of the ribbon (61) in
contact with, substantially tangential to the quench
surface (13) with respect to the take off point (49)
substantially parallel to, and at a velocity at least
20 2 times higher than the ribbon (61) velocity whereby
to apply tension to the ribbon (61) and increase the
duration of thermal contact between the ribbon (61)
and the chill surface (15).

25 2. The method of Claim 1 wherein the gas is
an inert gas.

3. The method of Claim 1 wherein the gas is
argon.

4. The method of Claim 1 wherein the quench
surface (13) means comprises circumferential heat sink
30 means (15).

5. The method of Claim 1 wherein the
disordered, filamentary material (61) is a hydrogen
storing material.

Case 820

-13-

6. The method of Claim 1 wherein the disordered, filamentary material (61) is a catalytic material.

5 7. The method of Claim 1 wherein the disordered, filamentary material (61) is a superconducting material.

10 8. The method of Claim 1 wherein the disordered material (61) is chosen from the group consisting of amorphous, materials, microcrystalline material, polycrystalline material, and mixtures thereof.

9. Quenching apparatus (1) carrying out the method of Claim 1 for forming a disordered filamentary material, (61) said apparatus comprising:

15 (a.) circular quench surface means (15);
(b.) container means (23) for molten material, said container (23) having discharge orifice means (21) in proximity to the quench surface (15), said quench surface means (15) being adapted to rotate
20 with respect to the discharge orifice means (21);

(c.) gas jet means (43) for providing a gas flow subsequent to the discharge (21) and the intended take off (49) of ribbon (61), tangential to the chill surface (15) at the take-off point of the ribbon (49),
25 and in contact with, substantially parallel to, and at a higher velocity than the ribbon (61) whereby to apply tension to the ribbon (61) and increase thermal contact between the ribbon (61) and the chill surface (15).

3.

FIG. 1

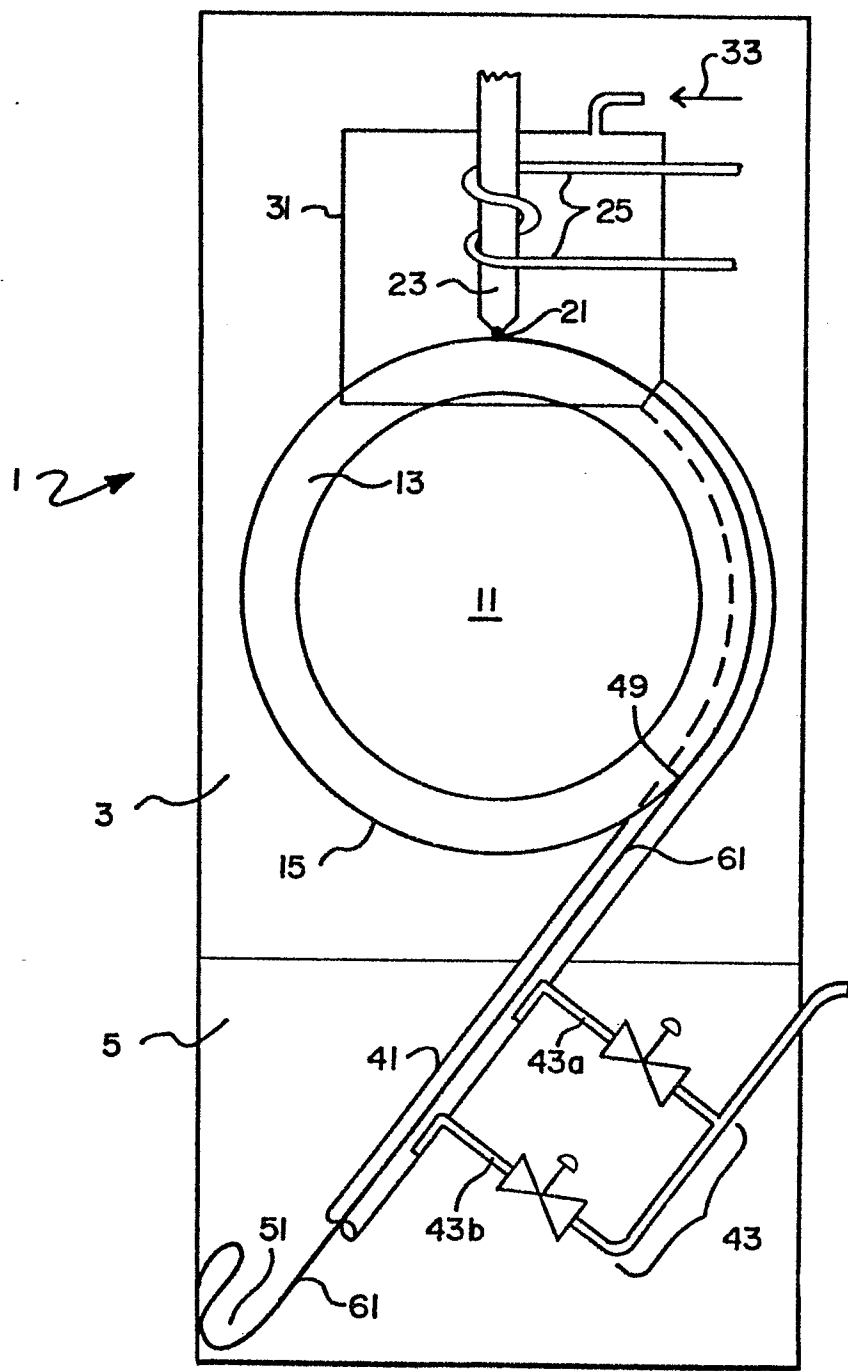


FIG. 2

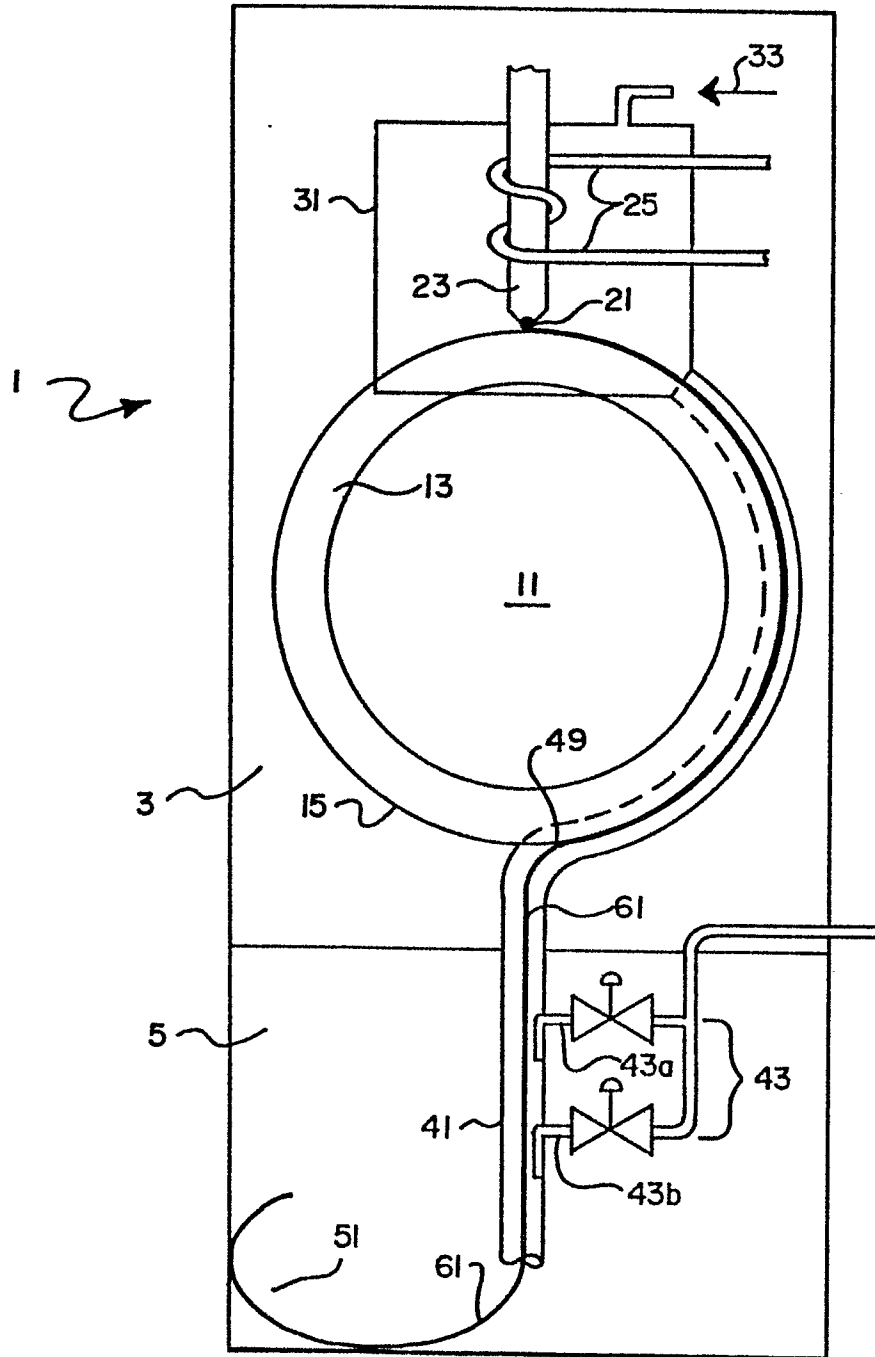


FIG. 3

