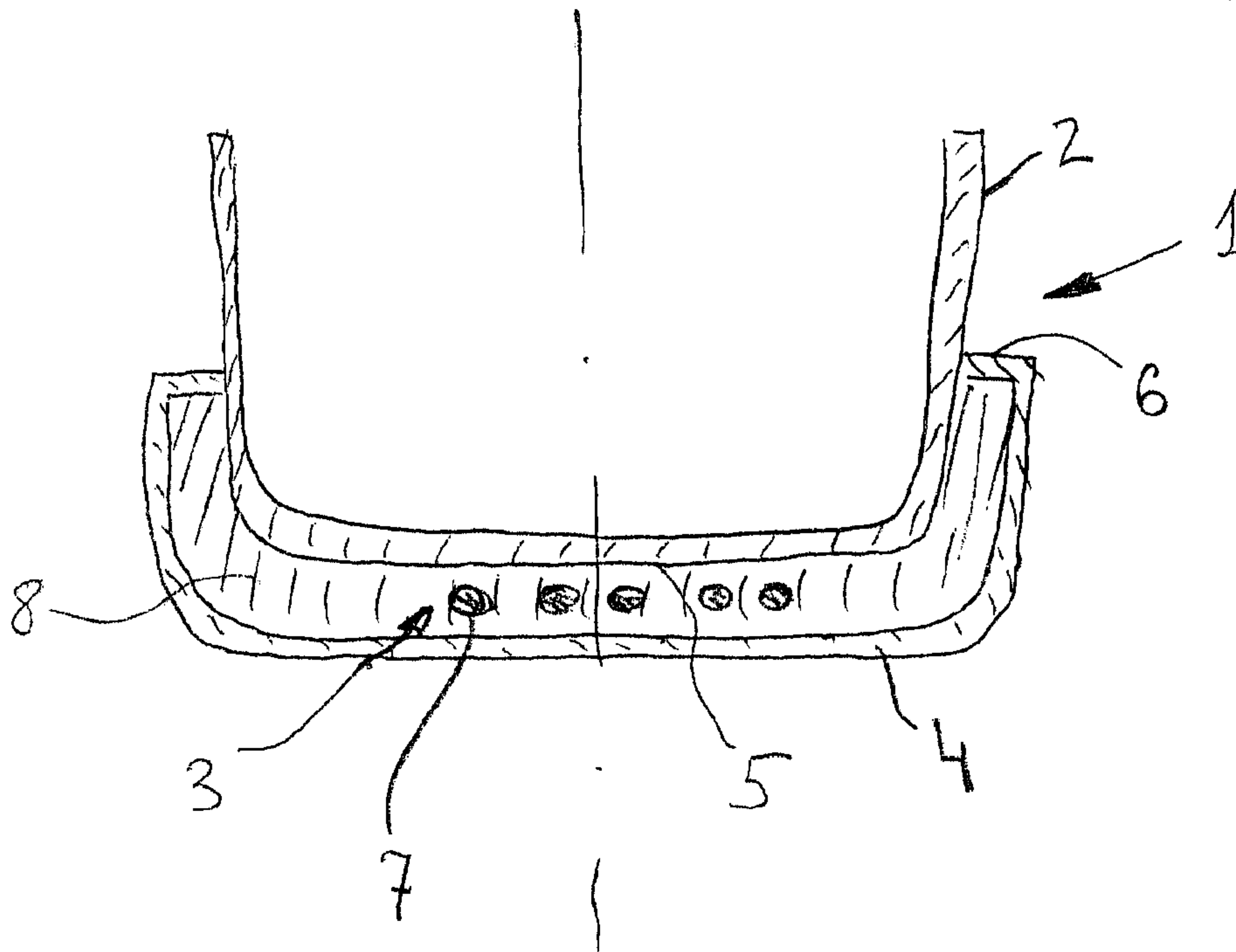




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 (72) Inventeur/Inventor:
 GOROKHOVSKY, VLADIMIR I., CA
 (73) Propriétaire/Owner:
 G & H TECHNOLOGIES LLC, US
 (74) Agent: GOWLING LAFLEUR HENDERSON LLP

(54) Titre : REGULATEUR DE TEMPERATURE POUR UN SUBSTRAT DANS LES PROCESSUS DE DEPOT PAR
 EVAPORATION SOUS VIDE
 (54) Title: TEMPERATURE REGULATOR FOR A SUBSTRATE IN VAPOUR DEPOSITION PROCESSES



(57) **Abrégé/Abstract:**

A heat transfer regulating mixture having a metallic component A with a melting point T_A and a particulate ceramic component B which is non-wettable by the metallic component A, non-reactive therewith and which has a melting temperature T_B which is higher than both the temperature T_A and a desired operating temperature T_D which is also higher than T_A . The metallic component A and the particulate ceramic component B and the respective amounts will typically be selected to have a higher thermal resistivity above T_A than below T_A . The heat transfer regulating mixture may be incorporated in the heat transfer regulating device having the mixture within an enclosure having first and second contact faces.

ABSTRACT

A heat transfer regulating mixture having a metallic component A with a melting point T_A and a particulate ceramic component B which is non-wettable by the metallic component A, non-reactive therewith and which has a melting temperature T_B which is higher than both the
5 temperature T_A and a desired operating temperature T_D which is also higher than T_A . The metallic component A and the particulate ceramic component B and the respective amounts will typically be selected to have a higher thermal resistivity above T_A than below T_A . The heat transfer regulating mixture may be incorporated in the heat transfer regulating device having the mixture within an enclosure having first and second contact faces.

TITLE: TEMPERATURE REGULATOR FOR A SUBSTRATE IN VAPOUR DEPOSITION PROCESSES

This application claims benefit of United States Provisional Application No.: 60/167,696,
5 filed November 19, 1999.

FIELD OF INVENTION

This invention is related to regulating the temperature of a substrate utilized in vapour deposition, in particular, in chemical vapour deposition.

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BACKGROUND OF THE INVENTION

Chemical and physical vapour deposition processes developed in the last few decades can produce high purity substances in commercial quantities. One of the more significant of such processes is, for example, the production of diamonds, usually in the polycrystalline state,
15 utilizing a plasma source. The production of diamonds by vapour deposition is accompanied by high thermal energy transfer. Should the heat transfer and substrate temperature regulation be inadequate, the crystallization and rate of growth of the deposit obtained, in particular, the uniform quality of the deposited diamond cannot be maintained. In other words, the temperature regulation and control of the substrate is a critical feature in both a
20 physical or a chemical vapour deposition (CVD) process. A frequently implemented method of substrate temperature control is regulating the heat loss of the substrate support or substrate mount means. Regulated heat loss of the substrate support or substrate mount is usually effected by conducting heat away in a controlled manner by some medium in contact with the substrate mount, as well as by regulating the heat removed by a heat sink. In U.S.
25 patent 5,527,392, issued to Snail et al. on June 28, 1996, a device for controlling the temperature of the substrate mount in a CVD reactor is described. A mixture of gases having such composition as to yield a desired mean thermal conductivity, is fed to the device, to flow at known flow rates about and around the substrate mount located in a housing. In addition, the geometry and the material of which the substrate mount is made of, are selected
30 to provide further control of the heat transfer capability of the substrate mount. The housing acts as the heat sink, and has means for a cooling fluid as well. One of the difficulties with

the above arrangement is that large and cumbersome gas tanks need to be installed to provide steady and reliable gas flows, as the heat control system is very sensitive to changes in the gas composition.

- 5 The metallurgical industries have been using sand or similar inert particles and air circulating between the particles in a vat or in a pile, for surrounding a large metal body which has been previously heated to a very high temperature, or for encasing a casting, to provide a particulate medium for controlled or slow cooling of the metal body or cast. There are known heat transfer methods utilizing multi-phase systems in other industries. For example,
- 10 U.S. PATENT 5,170,930, issued to T.P.Dolbear et al. on December 15, 1992, describes a liquid metal paste for utilization in fast cooling of electronic components and solid state chips. The semi-solid paste is made up of low melting metals and alloys, and solid particles of higher melting point materials, or in some instances, ceramic particles. The paste is required to have high viscosity, be both electrically and thermally conductive at temperatures
- 15 close to room temperature, and have additional characteristics specified useful in the electronics industry. It is noted that the primary function of the metal paste is to conduct heat away fast, and not to regulate the temperature of the electronic component at a certain level. Another multi-phase composition for fast cooling is described in U.S. PATENT 5,604,037, issued to J.-M. Ting et al. on February 18, 1997. The multi-phase composition comprises a
- 20 diamond/carbon/carbon fibre composite coated with a metallic layer for use as a dielectric heat sink in electronic systems.

In the above multi-phased cooling devices utilized by the electronics and metallurgical industries heat is removed, but no importance is attached to maintaining the temperature of

25 the system under consideration at a prerequisite level. There is a need for regulating the temperature of a substrate or the surface temperature of a substrate engaged in an exothermic reaction yielding a deposit, by regulating the heat loss by means of controlled heat transfer.

SUMMARY OF THE INVENTION

- 30 A heat transfer regulating mixture having a metallic component A with a melting point T_A and a particulate ceramic component B which is non-wettable by the metallic component A,

non-reactive therewith and which has a melting temperature T_B which is higher than both the temperature T_A and a desired operating temperature T_D which is also higher than T_A . The metallic component A and the particulate ceramic component B and the respective amounts will typically be selected to have a lower thermal resistivity above T_A than below T_A .

5

The metallic component A may be aluminum, tin, lead, gallium, indium, copper, silver and alloys thereof.

The particulate ceramic component B may be of alumina, titanium nitride, titanium carbide, titanium carbonitride, boron nitride, boron carbide, silicon carbide, silica and mixtures thereof.

The particulate component B may have an average particle size from 1 μm to 150 μm .

15 The heat transfer regulating mixture may be incorporated in the heat transfer regulating device having the mixture within an enclosure having first and second contact faces.

The heat transfer regulating device may be a cooking vessel, a shield wall, tube furnace or part of a substrate holder assembly for supporting a substrate body during a vapour
20 deposition process.

BRIEF DESCRIPTION OF THE DRAWINGS

Preferred embodiments of the present invention are:

25 Fig. 1a is a graphical representation of the influence of the melting point of a lower melting component A on the heat transferred from the substrate;

Fig. 1b shows the mean temperature of the substrate oscillating between a depositing temperature and the melting point of the lower melting component A;

30

Fig. 2 is a schematic representation of a substrate holder assembly according to the present

invention, including the heat transfer regulating composite mixture, and a multi-staged heat sink;

Figs. 3a and 3b are horizontal and cross-sectional views, respectively, illustrating a single
5 substrate holder arrangement according to the present invention;

Fig. 4a and Fig. 4b are horizontal and cross-sectional views, respectively, of a multi-substrate holder arrangement according to the present invention;

10 Fig. 5 is a graph illustrating the effect of the composition of a two-phase mixture of the present invention, on the temperature of a substrate used in a vapour deposition process;

Fig. 6 is a schematic representation of fry pan with bottom cavity filled with thermal regulating composite mixture according to the present invention;

15

Fig. 7a is a sectional view through a tube furnace incorporating a heat transfer regulating mixture according to the present invention;

Fig. 7b is an axial sectional view of an alternate embodiment of a tube furnace incorporating
20 a heat transfer regulating mixture according to the present invention;

Fig. 8 is a graph illustrating temperature versus time characteristics of a tube furnace according to Figure 7a or 7b;

25 Fig. 9 is a schematic illustration of a thermally resistant shield plate according to the present invention for use as a thermal barrier shield against impact with high temperature atmospheric flow at supersonic velocities;

Fig. 10 is a schematic illustration similar to Figure 9, but showing a substrate to be coated
30 and placed near a stagnation point of high temperature supersonic plasma flow; and,

Fig. 11 is an axial sectional schematic representation illustrating the use of a thermal regulating compound according to the present invention as a thermal regulating and support medium in a sliding bearing arrangement for supporting rotating parts exposed in a thermal transfer environment.

5

The preferred embodiments of the invention illustrated by examples will be described below.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The formation of a vapour deposited layer of a substance on a substrate is usually
10 accompanied by the generation of substantial amounts of heat. The generated heat needs to be removed, preferably at a controlled rate. If the heat generated is not removed in a controlled and regulated manner the vapour deposited layer can exhibit irregular morphology, internal stresses and uneven thickness, the substrate may develop cracks, or/and irregularities of similar nature may be encountered. One method of having a controlled heat transfer is to
15 encase or surround the substrate, including a substrate mount, in a medium which has a heat transfer coefficient λ , selected for the specific conditions of the vapour deposition process. In the instance of a multi-component system providing a heat energy removal means, the heat transfer coefficient λ can be computed as a mean value of the heat transfer coefficient of each component. It is to be noted, however, that the mean heat transfer coefficient derived for a
20 specific set of conditions of a vapour deposition process, cannot adapt itself to unforeseen and unexpected changes in the variables of the deposition process, or in other words, it does not usually provide automatic regulation of the temperature of the substrate.

For the sake of clarity, definition of what is understood by some of the terminology used in
25 the discussion of the preferred embodiment of the present invention is provided below.

"Substrate" is understood to mean a three dimensional body providing the surface on which the vapour species is deposited. Usually but not necessarily, only a portion of the surface, most frequently the surface in the proximity of one end of the substrate body, is utilized as
30 the depositing surface, and the other end of the body of the substrate is attached to or is supported by, a substrate mount or holder. It is preferred that the depositing surface of the

substrate has close to uniform temperature, while the rest of the substrate body is in a temperature gradient.

"Plasma" is considered to mean an atmosphere of low pressure and high temperature, containing ionized gaseous species. Not all the gases in the plasma are ionized, but it is usual that the species to be deposited is ionized. The components of a plasma often include argon or similar inert gases, both in the atomic state and in an ionized state. Other gases which may be utilized in a plasma are nitrogen, methane, oxygen, water, vaporized metal, short chained hydrocarbons, and similar gases which can take part in forming an element or a compound which is to be deposited. The plasma utilized in diamond or diamond-like coating deposition usually contains ionized methane gas.

"Heat sink" is commonly understood to mean a body or a series of bodies which remove heat predominantly by means of heat conduction or heat energy flow. A heat sink may be composed of several stages, each representing a certain thermal resistance manifested by a temperature gradient. A typical example of a heat sink stage is a metal body having water at ambient temperature circulated therethrough, in contact with another body at a higher temperature.

It has now been found that if a two-phase mixture is provided composed of a relatively low melting alloy or metal and a particulate ceramic material which conducts heat relatively well, an auto-regulating heat transfer system can be obtained. To obtain a satisfactory auto-regulating heat transfer system the metal or alloy should have a melting point preferably 200-800°C below the desired temperature of the depositing surface of the substrate, that is the temperature of the vapour deposition process, T_D . For obvious reasons, the melting temperature of the particulate ceramic material is usually substantially in excess of the temperature of the substrate. The selection of the ceramic material as a component of the two-phase mixture is governed by the process parameters. In other words, the melting point of metal or alloy forming the two-phase mixture in contact with the substrate is lower than the temperature at which the deposit is obtained, which is considerably lower than the melting temperature of the particulate ceramic. In general terms, if the mixture is made up

of component A and component B, having melting temperatures T_A and T_B , respectively, then for best results, the relationship $T_A < T_D < T_B$ has to hold. It is, however preferred, that the molten component A does not wet the particulate component B.

- 5 In the instance of depositing a microcrystalline layer of diamonds on a particular substrate the selected substrate depositing temperature T_D is around 900°C . The substrate is in contact or is encased, except for the depositing surface, by a mixture of a metal or alloy having melting point between 200°C and 700°C , and ceramic particles, such as alumina, TiN, SiO_2 in the form of sand or quartz, or a mixture of these substances. Other ceramic particles which
- 10 may be suitable as a component of the two-phase mixture of the present invention include boron nitride, boron carbide, silicon carbide, titanium carbide, high melting carbonitrides and oxynitrides, or chemical equivalents, and mixtures of such. The metal-ceramic particle mixture provides a semi-solid paste, or a highly viscous liquid bearing suspended solid particles, when in contact with the substrate at the temperature of the vapour deposition
- 15 process, such as deposition of diamonds. When the heat is removed too fast, or the substrate temperature drops below the desired temperature, the two-component mixture freezes or solidifies, leading to poor or uneven contact between the mixture and the substrate. The effect on the heat removed, of the melting temperature of the lower melting component in the two-phase mixture in the neighbourhood of its melting point, is shown schematically in
- 20 Fig. 1a, where R_{TC} is the thermal contact resistance of the two component mixture, expressed as $\text{cm}^2 \cdot ^\circ\text{C}/\text{watt}$, and T_A is the melting point of the lower melting component, usually a metal. It can be seen that the thermal resistance has a low value when the mixture in thermal contact with the substrate, is composed of a liquid metal and a suspension of ceramic particles, resulting in high heat flux. The high heat flux lowers the temperature of the substrate in
- 25 contact with the mixture, leading to the freezing of the mixture, thus severing contact between the mixture and the substrate, thereby increasing the thermal resistance and lowering the value of heat flux, or the rate of heat transfer per unit area. Lower heat flux or lower rate of heat transfer from the substrate results in an increase in the substrate temperature, which in turn, leads to the remelting of the two-component mixture and to the restoration of heat
- 30 removal rate to the previous level. Thus the heat flux from the substrate, and hence the substrate temperature (T_{st}), will oscillate around an average value T_p , between the depositing

temperature T_D and the melting point T_A , of the metallic component of the two-phase mixture, as shown schematically in Fig. 1b, and can be described by the inequality $T_A < T_P < T_D$.

In the preferred embodiment of the invention, the substrate has a portion of its surface pre-
 5 treated to be able to receive the vapour deposited species. The pre-treatment usually includes mechanical and conventional cleaning process steps, and other known treatments to render the substrate surface receptive of the deposited species. The substrate is usually mounted in a substrate holder or mount, supported on a base or housing, which is immersed in an atmosphere containing the vapour to be deposited. As discussed above, the substrate is
 10 encased or is surrounded below the pre-treated portion of the surface, by a physical mixture of a low melting point metal or alloy and small sized particles of a ceramic material. The base supporting the substrate is usually made of metal, which represents the first stage of a conventional heat sink. Depending on the dimensions and on the nature of the base, the first stage of the heat sink has a certain thermal resistance, R_1 . In the most simple case, the heat
 15 sink has only one stage, providing heat transfer between the substrate, the temperature of which is close to the melting temperature T_A of the lower melting component of the two-phase mixture, and the exit temperature T_L of the cooling liquid or fluid, circulating in the housing supporting substrate base. Thus $R_1 \sim (T_A - T_L) / Q$, where Q is the heat flux measured in watts per cm^2 , ($\text{w} \cdot \text{cm}^{-2}$), and R_1 has dimensions $\text{cm}^2 \cdot ^\circ\text{C} / \text{w}$. For example, when $Q = 100$
 20 $\text{w} \cdot \text{cm}^{-2}$, and $(T_A - T_L)$ is 500°C , the value of the thermal resistance R_1 is close to $5 \text{cm}^2 \cdot ^\circ\text{C} / \text{w}$.

In more complex designs, the substrate base and the housing incorporating the base, may be supported on another metal block incorporating circulating oil or a similar cooling fluid, thus providing the second stage of a conventional heat sink arrangement, having a second thermal
 25 resistance, R_2 . The last stage of the heat sink is frequently, however, not necessarily, another conventional water cooled metal structure, providing yet another thermal resistance R_3 . Thus the heat sink channels the heat transferred through several stages of thermal resistance to the ambient temperature in a conventional manner. A schematic representation of the preferred embodiment of the present invention is shown on Fig. 2. An assembly 10, utilized in a vapour
 30 deposition process contains an elongated substrate body 14, having a depositing surface 12, which is immersed in a high temperature atmosphere 26, containing the species to be

deposited. A stem 18, of the substrate 14 is held in a substrate mount or substrate holder 20, which is in contact with or is supported on a substrate mount base 22. The supporting base 22, and the substrate mount 20, may constitute a single entity or may be separate units. The assembly has a water cooled base 24, in direct contact with ambient temperature. The
5 substrate stem 18 is surrounded by a composite two-phase mixture 16, composed of a low melting metal A, of melting point T_A , and a particulate ceramic material B, non-wetted by A, having melting point T_B well in excess of the depositing temperature T_D . In the instance of diamond deposition, the atmosphere in which the substrate is immersed, is a plasma bearing ionised carbon. A convenient plasma composition for diamond deposition is a
10 mixture of methane gas, hydrogen and an inert gas, such as argon. When the vapour deposited layer attains a desired thickness the substrate is removed from the vapour bearing atmosphere, or in this particular process, from the ionised carbon containing plasma, and a fresh substrate is placed in the depositing chamber.

15 The metal in the two-component mixture can be tin, lead, aluminum, indium, gallium, copper-silver alloy, and an alloy of these metals, or any other similar low melting metal or alloy which is not affected by the surrounding atmosphere. The particle size of the metal before melting is not critical, but to ensure good mixing the particle size of the metal powder is preferably between 1 and 10 μm . As has been mentioned above, the particulate ceramic
20 may be one or a mixture of alumina, silica, titanium nitride, titanium carbide, titanium carbonitride, boron carbide, boron nitride or materials which have high melting temperature, are oxidation resistant, are also relatively good heat conductors and are not wetted by the metal in combination with they are used. The average particle size is dictated by convenience and is usually less than 1 μm .

25

The composition and the ratio of the low melting metal or alloy component to the ceramic component in the two-phase mixture is determined by the nature of the deposited coating, the desired coating thickness, the ultimate purpose of the vapour deposition process, the size of the substrate, the temperature of the vapour depositing reaction and similar process
30 considerations. The convenient ratio in weight, of the low melting metal or alloy to the ceramic particles ranges between 10:90 and 80:20.

The pre-treatment of the depositing surface of the substrate can include usual process steps such as grinding, polishing, cleaning, preheating, etching, ion cleaning, ion nitrating, coating with a non-reactive layer, priming of the surface and treatment by radiation.

5 A single substrate holder assembly and its cross-section at the substrate stem level is illustrated in Figs. 3a and 3b. The substrate carrying assembly 30, has a substrate holder base 32, a housing 34, a substrate holder O-ring 35, a substrate mount 36, which is designed to hold a substrate 40, and a two-phase composite mixture 38 of the present invention. The substrate 40, having a depositing surface 42, is held in contact with the two-phase mixture
10 38, within the mount 36. A substrate mount support 55, is a metal tubing which supports substrate mount 36, and also serves as a means to transfer heat energy to the various heat sink stages. The cross-section of the substrate mount 36 is shown in Fig.3b, where like items are indicated by like reference numerals.

15 A multi-substrate holder 50 is shown in Fig.4a, and its cross-sectional view in Fig.4b. The multi-substrate holder assembly 50, has components similar to the single substrate holder assembly 30, of Fig.3a, indicated by reference numerals 32, 34, 35, 36, and 55. The two-phase mixture 38 in this case is in contact with a plurality of substrate stems 44, arranged in a circle around a mount seal 46. A cross-sectional view of the substrate mount 36, having
20 substrate stems 44 in a circular formation, packed with the two-phase mixture 38, and held in position by the mount seal 46, is shown in Fig.4b.

The plasma creating gas in the vapour depositing processes utilizing the two phase composite mixtures for regulating the temperature of the vapour deposition may include one or more
25 of nitrogen, methane and similar short chained hydrocarbon, oxygen, hydrogen, water, inert gases, and vaporized metal.

EXAMPLE 1

Metal rods of 2mm diameter, made of tungsten alloyed with 2wt% lanthanum, were cut into
30 19mm lengths, to be made into dental drills by coating each 19mm rod with a layer of vapour deposited polycrystalline diamond. The metal drill substrates to be coated were first

mechanically polished by sandblasting with silicon carbide of 100 μ m size, cleaned ultrasonically in an acetone bath, and then the surface to be coated was primed by dipping into a isopropyl alcohol suspension of submicron sized diamonds to provide seeding.

- 5 Composite mixtures were made of fine tin of particle size 1-5 μ m and boron nitride having particle size less than 1 μ m. The tin content of the composite mixtures were as follows: 20%, 40% and 80%, and an additional test with no tin added.

Twelve (12) pretreated drill substrates for vapour deposition were placed in a multi-substrate
10 holder 36, as shown in Fig.4, packed with one of the above tin-boron nitride composite mixtures for controlling and regulating thermal energy transfer, and the drills surrounded by the composite mixture were held in position by the mount seal 46. The substrate holder with 12 drills, was subsequently placed in an arc assisted CVD reactor, such as for example, described in United States patent No. 5,587,207, to be coated with vapour deposited,
15 polycrystalline diamond coating. The gas in the reactor was composed of argon, hydrogen and methane in a ratio: Ar:H₂:CH₄ = 2000:500:4. The temperature of the substrate holder during vapour deposition was measured by means of a precision thermocouple brazed to one of the drills held in the substrate holder. The power flux proceeding from the arc plasma column towards the substrate surfaces was 10watt.cm⁻². The duration of each diamond
20 coating deposition utilizing two phase composite mixtures of different tin content was 12 hours.

The temperature of the substrate holder during the vapour deposition process was plotted against the tin content of the two phase mixture surrounding the drills, starting with pure
25 boron nitride powder. The results are shown on Fig.5. It is noted, that in the absence of tin in the thermal energy transfer regulating substance high but rapidly fluctuating temperatures were observed, and the diamond coating obtained was uneven, having irregular crystallite sizes. Another variable tested in the above vapour deposition process having controlled and regulated thermal energy transfer means, was the pressure within the depositing chamber.
30 However, as it can be seen, variations in the pressure between 6 and 15 torr had no effect on the substrate holder temperature. The quality and morphology of the coating obtained was

examined by scanning electron microscopy (SEM). It was found that a two phase composite mixture containing 20% tin and boron nitride provided the optimum conditions for obtaining uniform polycrystalline coating of even sized diamonds at a high deposition rate of 3 μ m per hour.

5

EXAMPLE 2

A sintered tungsten carbide-6% cobalt containing insert of 3mm height and having a 10mm by 10mm square face to be coated with diamond coating, was placed in a single substrate holder assembly shown on Fig.3. The surface of the carbide insert was pre-treated by SiC
10 sandblasting and ultrasonic cleaning as described in Example 1, then etched in a solution of 1:1 HCl-H₂SO₄, followed by seeding in a submicron sized diamond suspension in isopropyl alcohol. The pre-treated carbide inserts were individually coated utilizing different tin-boron nitride mixtures as the thermal energy transfer regulating two phase composition. The temperature of the substrate was measured by a thermocouple attached to the underside of
15 the sintered carbide insert. The thermal energy transfer regulating two phase BN-tin compositions included 20% and 40% tin, as well as boron nitride without tin addition for comparison. The size of the boron nitride particles was less than 1 μ m, and the admixed fine tin had particle size ranging between 1 μ m and 5 μ m. The diamond coating was obtained in a CVD apparatus, and under conditions similar to that described in Example 1. It was found
20 that using boron nitride powder only as thermal energy transfer regulating packing, resulted in irregular substrate temperatures, and no or only very poor quality diamond coatings could be obtained. Polycrystalline diamond coatings of desired quality, composed of even sized diamond crystallites of 20-30 μ m, were obtained with 40% tin containing BN-tin mixtures as the two phase compositions. The average rate of diamond deposition under such
25 conditions was 3.5 μ m per hour.

EXAMPLE 3

Razor blades coated with a "diamond-like-carbon" coating were obtained by a vapour depositing process referred to as DLC coating process. The diamond-like-carbon coatings
30 were produced in an apparatus utilizing filtered cathodic arc carbon plasma, such as for example, described in United States patent No. 5,435,900, and operated at 10⁻⁵ torr pressure.

The steel blades to be coated were attached to the surface of a well polished, massive block of aluminum. The aluminum block was water cooled. To obtain uniform DLC coating it was essential that the thermal energy generated by vapour deposition was transferred in a regulated manner by a thermally conductive compound. One face of the thin steel blades was
5 in contact with the aluminum block by means of a thin layer of a two phase composition containing 40% gallium of particle size 45 to 60 μ m, in a Ga-BN mixture. The Ga-BN mixture was first suspended in iso-propyl alcohol and painted on the surface of the aluminum block to form a coating under the thin steel blades prior to applying vapour deposition. The nano-hardness of the DLC coating obtained using the two-phase Ga-BN mixture as thermal
10 energy transfer regulating medium, was measured to be 60 GPa. In comparison, vapour deposited DLC coatings on steel razor blades were obtained without the utilization of thermal energy transfer regulating compositions of the present invention. The resulting coatings were uneven and when tested exhibited substantially lower nano-hardness.

15 The above examples describe the utilization of two phase mixtures of low melting metal-ceramic particles in processes for obtaining diamond or diamond-like-carbon coatings. The thermal energy transfer regulating mixtures may be used in other processes, chemical or physical, for obtaining vapour deposited coatings of even grain size and thickness. It will also be apparent that the method of regulating thermal energy transfer described herein can
20 be applied to many other types of processes for obtaining vapour deposited coating beyond the examples given, for instance, coatings of ceramic materials, such as tungsten carbide, and other hard wearing ceramic materials on hard metal surfaces deposited at elevated temperatures. The operational parameters, such as the temperature difference between the deposition and the substrate base, composition of the two phase mixture, gas composition
25 bearing the vapour to be deposited, vapour pressure of the depositing species etc. are adjusted according to the desired coating.

The method of regulating heat and energy transfer by utilizing a two phase mixture of high melting point ceramic particles and a low melting point metal can be applied in
30 manufacturing processes in fields other than vapor deposition, such as the manufacture and use of cooking utensils or pots, tube furnaces and thermal barrier shield for jets and rockets

as described below. It can also be utilized in such other applications as sintering by powder metallurgy, heat treatment and ion nitrating, for heat sink devices in electronics, thermal insulation in building construction, food processing, thermal regulating in biological environments and in medical applications.

5

EXAMPLE 4

Cooking pots or similar utensils, made of stainless steel or other suitable metals and having convenient size and volume can be manufactured utilizing the heat transfer regulating mixture of the present invention. It is a known practice to have a stainless steel flat bottomed container equipped with a relatively high heat capacity aluminum, copper or stainless steel
5 plate. In conventional cooking pots the plate has a rim adapted to smoothly enclose the circumference of the container and attached to the flat bottom of the container by means of high temperature soldering, brazing or similar conventional methods. The role of the aluminum, copper or stainless steel plate is to ensure even and rapid heat transfer from an electrically heated hot plate or cooking ring or a gas-burning device, in a normal cooking or
10 household heating operation. One of the shortcomings of such a conventionally attached plate to the bottom of the container is that it allows relatively rapid heat loss, in other words, the contents of the container, e.g. the food cooked, will cool rapidly which may be undesirable.

Fig.6 shows schematically a cooking utensil or pot 1, made of conventional parts, that is a
15 stainless steel container 2, having a flat bottom section 5, tightly fitting into a heavy gauge stainless steel base cap 4, having a rim 6, adapted to enclose the container 2. A cavity 3 is defined between the container 2, and rimmed base cap 4, is filled with a composite mixture 8, according to the present invention, having the following composition: 40 wt % indium powder, of -325 mesh (less than 40 μ m) size, thoroughly mixed with 60 wt % boron nitride
20 ceramic powder of 5 μ m particle size. When placed on a gas ring or conventional hot plate of a stove, the three component cooking pot 1, can be used as a cooking utensil in the usual manner. At the melting temperature of indium, 156°C, the composite mixture becomes a two phase semi-solid mixture with excellent heat conducting or heat transferring properties ensuring rapid heating of the contents of the vessel.

25

When a heating process using the cooking pot 1 shown on Fig.6, is terminated, that is the contents of the cooking pot have been maintained at the prerequisite temperature for a prerequisite period of time, the heat is turned off, resulting in the gradual cooling of the cooking pot and its contents. When the temperature inside cavity 3, drops below the melting
5 point of indium, the liquid indium solidifies, the ceramic powder becomes dispersed in the solidified metal, leading to a substantial slowing down in the rate of further heat transfer, that is the cooling of the contents of the vessel. In other words, the contents in the cooking pot can be kept warm longer.

10 In an other embodiment of the present invention a heater such as shown by representative heating elements 7 can be incorporated in the bottom of the cooking pot, surrounded by the thermal regulating compound 3.

EXAMPLE 5

15 Thermal regulating compound can be used as a thermal transfer medium for tube furnaces and related CVD reactors. A high temperature tube furnace 100 is schematically shown in Figure 7a. It consists of a tubular furnace body 102, created by two tube liners, external liner 103 and internal liner 104. A thermal regulating compound 105 according to the present invention fills the space between the tubes 103 and 104. In this case the thermal regulating compound 105
20 consists of 20% weight of copper powder with particle size 3-5 μm as a component A having low melting point ($T_A \sim 1050^\circ\text{C}$) and balance fine alumina powder with particle size 1-2 μm as a component B having a high melting point. The tubular body 102 is surrounded by a heating array 106, made of molybdenum and an external thermal insulating tube 107, having an internal reflecting surface 108. The molybdenum heaters 106 are heated by DC current,
25 provided by a DC power supply (not shown). At a moment t_{on} when the heaters are turned on, a thermal flux q is directed on the external surface of the tubular body 102. When the temperature of the thermal regulating compound exceeds the melting point of copper T_A , the copper will melt and the thermal resistivity of the tubular body 102 will drop down to the level determined by the low melting point component A. The temperature inside the furnace will
30 increase rapidly to exceed the melting point of copper. If the heaters are turned off at a moment t_{off} , the temperature of the tubular body will decrease quickly below the melting point

T_A . At that moment the copper will solidify and the thermal resistance of both the thermal regulating compound 5 and the entire tubular body 2 will increase to the level, determined by the ceramic component B. From this moment the temperature inside of the furnace will decrease very slowly due to the thermal insulating properties of the ceramic component B of the thermal regulating compound 5 as it is diagrammatically shown in Fig. 8. It can be seen that heat can easily propagate from the outside toward the inside space of the furnace throughout the furnace body 2 during the heating stage, while it keeps insulated and trapped during the cooling stage when the heating array 106 is turned off.

10 In an other embodiment, and as shown in the axial section view of Figure 7b, a heater array 153 can be incorporated in the body of a furnace 150, surrounded by a thermal regulating compound 152 for heating gas flow. In this case the furnace body consists of a tubular enclosure 151 filled with a thermal regulating compound 152. A conventional ceramic thermal insulation 154 surrounds outer surface of the furnace body 151. Both ends of the furnace are
15 sealed by respective ceramic lids 156 and 157. The lid 157 has a discharge nozzle 159 and the lid 156 has an inlet pipe 158 for injecting a gas mixture 160 respectively to be heated in the furnace 150.

EXAMPLE 6

20 The thermal regulating compound can be successfully used as a thermal barrier shield against impact with high temperature atmospheric flow for supersonic jets and space rockets. The change in concentration of low melting point component A allows one to regulate the thermal resistance of the shield with a high degree of accuracy, as was shown above in Figure 5 for the CVD processing of polycrystalline diamond coatings. An arrangement 200 for modeling
25 thermal transfer between high temperature supersonic air plasma flow and a thermally resistant shield plate is schematically shown in Figure 9. It consists of a flat shield-wall 202, having two parallel inconel plates: a front plate 203 and a back plate 204. A thermal regulating compound 205, having the same composition as in Example 5 fills the space between plates 203 and 204. A source 206 of a supersonic high temperature jet 211 is installed
30 in front of the shield 202. It consists of a supersonic nozzle 207, a gas inlet 208 and a resistance heater 209 connected to a DC power supply (not shown). A back side of the shield

is cooled by a forced convection means 210. When the supersonic high temperature jet 211 is directed on the shield 202 the temperature of the thermal compound increases and eventually reaches the melting point of the component A. At this moment the thermal resistance of the shield drops down to allow it to protect the front plate 3 against excessive thermal flux coming from the supersonic jet 211. When the oncoming thermal flux decreases, the low melting point component solidifies and thermal resistance of the shield 202 increases which keeps the temperature of the front plate 203 high providing preferable conditions for radiation cooling.

10 This arrangement can be also used as a supersonic jet assisted CVD reactor as shown in Figure 10. In this case a carbide insert 212 as a substrate to be coated is placed near the stagnation point of high temperature supersonic plasma flow on the front surface of the shield 202. The plasma creating gas composition consists of argon (3 slm), hydrogen (0.5 slm) and methane (3 sccm). The thermal regulating compound 205, contains 1-5 μm size BN powder with a 3-5 μm size 20 weight % aluminum powder composition allows the temperature on the surface of the carbide insert 212 to be kept at 900°C with an accuracy of +/- 2%.

EXAMPLE 7

A two-phase thermal regulating compound according to the present invention can be used as a thermal regulating and support medium in a sliding bearing arrangement to support rotating parts exposed in a thermal transfer environment. Fig 11 shows a rotating shaft 301 with a heat receiver 302 supported by a radial bearing 303, consisting of a cylindrical body 304 with external cooling ribs 305 made of steel and with two opposed graphite lids 306. The cavity created by the body 304 and the lids 306 is filled with a thermal regulating compound 307 having the same composition as in Example 1. The shaft 301 is rotated by a conventional motor (not shown). When the temperature of the shaft 301 exceeds the melting point of low melting point component of the thermal regulating compound 307 (tin) this component melts, providing an increase in the thermal conductivity in the vicinity of the shaft 301 and a simultaneous reduction in the friction between the shaft 301 and the surrounding thermal regulating compound 307.

While the above examples have referred to specific ratios of the low melting point component to the particulate ceramic component, it will be appreciated that strict adherence to the specific ratios is not essential. It is expected that typically the thermal regulating compound (heat transfer regulating mixture) may have from 20 to 80% by weight of the metal with the balance
5 being the ceramic component. It is further expected that a more preferred range will have from 40% to 60% of the metal component.

The foregoing has described the principles, preferred embodiments and modes of operation of the present invention. However, the invention should not be construed as limited to the
10 particular embodiments discussed. Instead, the above-described embodiments should be regarded as illustrative rather than restrictive, and it should be appreciated that variations may be made in those embodiments by workers skilled in the art without departing from the scope of the present invention as defined by the following claims.

I CLAIM:

1. The use in a heat transfer regulator of a mixture comprising:
a metallic component having a melting point T_A ; and,
a particulate ceramic component which is non-wettable by the metallic component,
non-reactive therewith and has a melting temperature T_B which is higher than both the temperature T_A and a pre-determined operating temperature T_D which is also higher than T_A ; wherein said metallic component undergoes a phase change between its solid and liquid phases thereby changing the thermal resistivity of said mixture as part of a temperature regulating function.
2. The use in a heat transfer regulator of a mixture according to claim 1 wherein the metallic component, the particulate ceramic component and their respective amounts are selected to yield a lower thermal resistivity above T_A than below T_A .
3. The use in a heat transfer regulator of a mixture as claimed in claim 2 wherein the metallic component is selected from the group consisting of aluminum, tin, lead, gallium, indium, copper, silver and alloys thereof.
4. The use in a heat transfer regulator of a mixture as claimed in claim 2 wherein said particulate ceramic component is selected from the group consisting of alumina, titanium nitride, titanium carbide, titanium carbonitride, boron nitride, boron carbide, silicon carbide, silica and mixtures thereof.
5. The use in a heat transfer regulator of a mixture according to claim 4 wherein said particulate component has an average particle size of from $1\mu\text{m}$ to $150\mu\text{m}$.
6. The use in a heat transfer regulator of a mixture according to claim 4 wherein said metallic component is selected from the group consisting of aluminum, tin, lead, gallium, indium, copper, silver and alloys thereof.
7. The use in a heat transfer regulator of a mixture according to claim 6 wherein said particulate component has an average particle size of from $1\mu\text{m}$ to $150\mu\text{m}$.

8. A heat transfer regulating device comprising:

an enclosure having first and second contact faces;

a heat transfer regulating mixture within said enclosure which is selected to correspond to a pre-determined operating temperature T_D , said heat transfer regulating mixture including a metallic component having a melting point T_A and a particulate ceramic component having a melting point T_B above the melting point T_A and above the pre-determined operating temperature T_D ;

said ceramic component being non-reactive with and non-wettable by said metallic component; and,

said mixture having a thermal restivity which is lower above T_A than it is below T_A by virtue of melting of said metallic component.
9. A heat transfer regulating device as claimed in claim 8 wherein the metallic component is selected from the group consisting of aluminum, tin, lead, gallium, indium, copper, silver and alloys thereof.
10. A heat transfer regulating device as claimed in claim 8 wherein said particulate ceramic component is selected from the group consisting of alumina, titanium nitride, titanium carbide, titanium carbonitride, boron nitride, boron carbide, silicon carbide, silica and mixtures thereof.
11. A heat transfer regulating device as claimed in claim 10 wherein said particulate ceramic component has an average particle size of from $1\mu\text{m}$ to $150\mu\text{m}$.
12. A heat transfer regulating device as claimed in claim 10 wherein said metallic component is selected from the group consisting of aluminum, tin, lead, gallium, indium, copper, silver and alloys thereof.
13. A heat transfer regulating device as claimed in claim 12 wherein said particulate ceramic component has an average particle size from $1\mu\text{m}$ to $150\mu\text{m}$.

14. A heat transfer regulating device as claimed in claim 8 wherein said enclosure has oppositely disposed first and second sides;

said first face is on said first side; and,

said second face is on said second side.
15. A heat transfer regulating device as claimed in claim 14 wherein said first and second sides are of metal.
16. A heat transfer regulating device as claimed in claim 15 wherein:

said first side is a bottom inner face of a cooking vessel;

said metallic component is indium; and,

said particulate ceramic component is boron nitride.
17. A heat transfer regulating device as claimed in claim 16 wherein:

said indium is initially less than 40 μm sized particles;

said boron nitride is of less than 5 μm particle size; and,

said indium and said boron nitride are present in said heat transfer regulating mixture in a proportion of from 20% to 80% by weight indium with the balance being boron nitride.
18. A heat transfer regulating device as claimed in claim 15 wherein:

said first side is an external liner of tubular furnace body; and,

said second side is an internal line of a tubular furnace body.
19. A heat transfer regulating device as claimed in claim 18 wherein:

said metallic component of said heat transfer regulating mixture consists of copper; and,

said particulate ceramic component consists of alumina.

20. A heat transfer regulating device as claimed in claim 19 wherein:
said copper has an initial particle size of from 3 to 5 μm ;
said alumina has a particle size from 1 to 2 μm ; and,
said copper and said alumina are present in amounts of 20% by weight copper and 80% by weight alumina.
21. A heat transfer regulating device as claimed in claim 15 wherein:
said first side is a front plate of a shield wall; and,
said second side is a rear plate of a shield wall.
22. A heat transfer device as claimed in claim 21 wherein:
said metallic component is aluminum, initially of a 3-5 μm particle size powder; and,
said particulate ceramic component is boron nitride having a particle size of from 1-5 μm .
23. A heat transfer regulating device according to claim 22 wherein:
said aluminum and said boron nitride are present in amounts of 20% by weight aluminum and 80% weight boron nitride.
24. A heat transfer regulating device as claimed in claim 22 wherein said aluminum and said boron nitride are present in said heat transfer regulating mixture in amounts of from 20% to 80% by weight aluminum with the balance being boron nitride.
25. A substrate holder assembly for supporting a portion of a substrate body during a vapour deposition process at a temperature T_D , said substrate holder assembly comprising:
a substrate mount having a receptacle for receiving a stem of said substrate body; and,
a supporting base for supporting said substrate mount ; wherein

a space between said stem and said substrate mount is filled with a heat transfer regulating mixture having,

a metallic component with a melting point T_A ; and,

a particulate ceramic component with a melting point T_B ,

such that $T_A < T_D < T_B$ and said metallic and ceramic components are non-wetting and non-interacting at T_D .

26. A substrate holder assembly as claimed in claim 25, wherein said particulate ceramic component has an average particle size of from between $1 \mu\text{m}$ and $150 \mu\text{m}$.
27. A substrate holder assembly as claimed in claim 25, wherein said metallic component is selected from the group consisting of aluminum, tin, lead, gallium, indium, copper-silver alloy, and alloys thereof.
28. A substrate holder assembly as claimed in claim 25, wherein said particulate ceramic component is selected from the group consisting of alumina, titanium nitride, titanium carbide, titanium carbonitride, boron nitride, boron carbide, silicon carbide, silica and mixtures thereof.
29. A substrate holder assembly as claimed in claim 25, wherein said metallic component and said particulate ceramic component are present in a weight ratio of from 10:90 and 80:20.
30. A substrate holder assembly as claimed in claim 25, wherein said pre-treated portion of said surface has been pre-treated by one of the methods selected from the group consisting of sandblasting, grinding honing, polishing, lapping, treatment in a vibratory bowl filled with abrasive media, pre-heating, etching, ion cleaning, ion nitrating, ion implantation, ion coating deposition of buffer interlayer and treatment by radiation.
31. A substrate holder assembly as claimed in claim 25, wherein said atmosphere containing vaporized species contains of one or more gaseous substances selected from the group

- consisting of nitrogen, methane, argon, inert gases, oxygen, water, vaporized metal and short chained hydrocarbons.
32. A substrate holder assembly as claimed in claim 25, wherein said vapour deposited substance is diamond and said atmosphere of vaporized species is ionized carbon bearing plasma.
33. A heat transfer regulating assembly for use in a vapour deposition process, comprising:
- i) a substrate body having a surface, a portion of said surface having been pre-treated to receive a vapour deposited substance at temperature T_D , said substrate body being removably held in a substrate mount supported on a substrate base, and said substrate surface being exposed to an atmosphere comprising species of vaporized components of said substance,
 - ii) a first mixture comprising component A, having melting point T_A , and component B, having melting point T_B , such that $T_A < T_D < T_B$, wherein said components A and B are non-interacting at T_D , and said first mixture is in contact with said substrate body below said pre-treated portion of said surface, and,
 - iii) a heat sink incorporating said substrate base, and having at least one stage capable of transferring heat to a lower temperature, and each stage having a thermal resistance.
34. A heat transfer regulating assembly for use in a vapour deposition process as claimed in claim 33, wherein said heat sink has a plurality of stages, and the final stage has fluid at ambient temperature circulating therethrough.
35. A heat transfer regulating device for use in a vapour deposition process as claimed in claim 14 wherein:
- registering openings are provided in said first and second faces;
 - a rotatable shaft extends through said registering openings and through said heat transfer regulating mixture; and,

a heat receiver is provided at an end of said shaft.

36. A heat transfer regulating device as claimed in claim 35 wherein:

a cylindrical body extends between said first and second faces;

said cylindrical body is of metal and provided with radially outwardly extending cooling ribs; and,

said first and second faces are on respective graphite lids.

[TOR_LAW5450694\2]

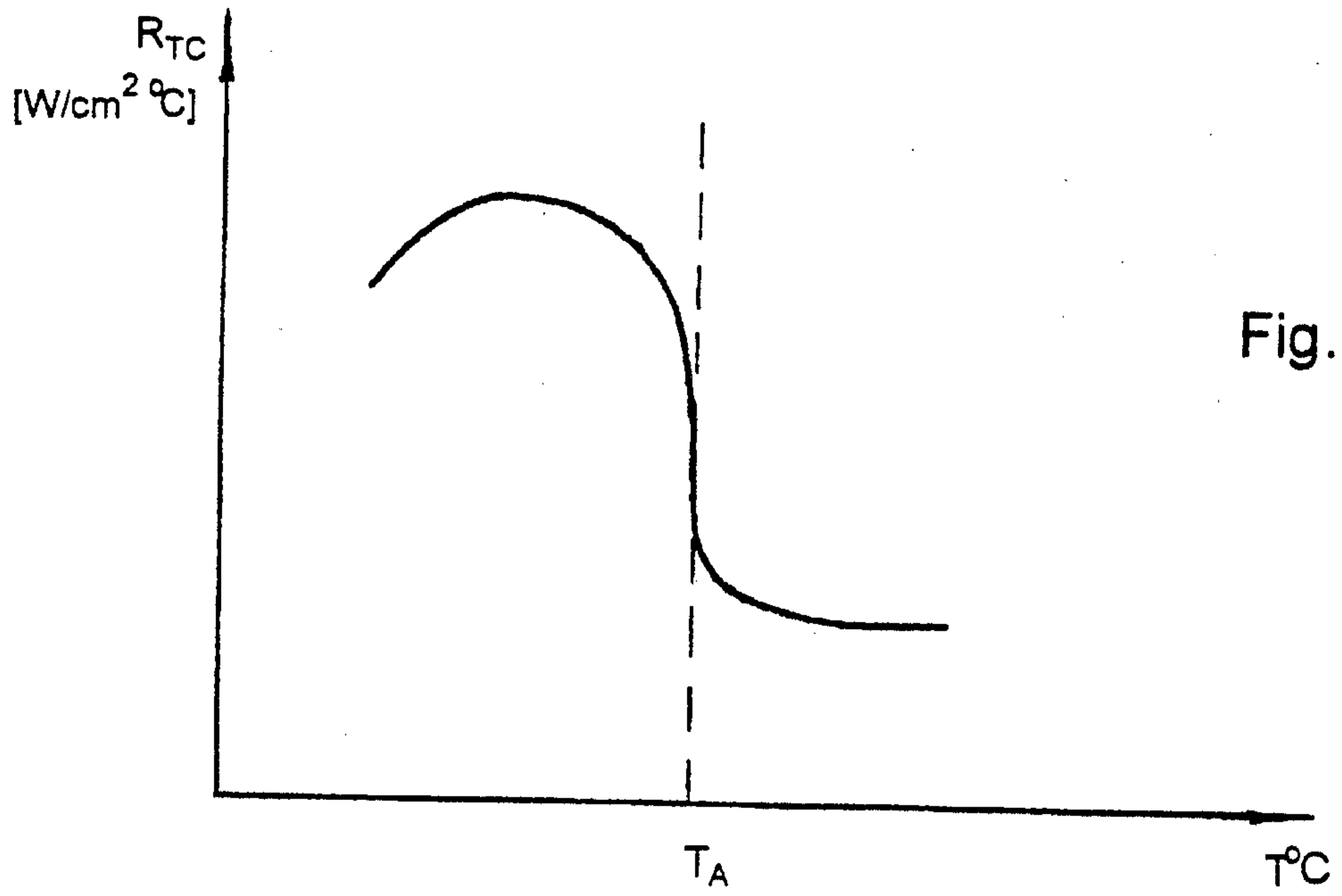


Fig. 1a

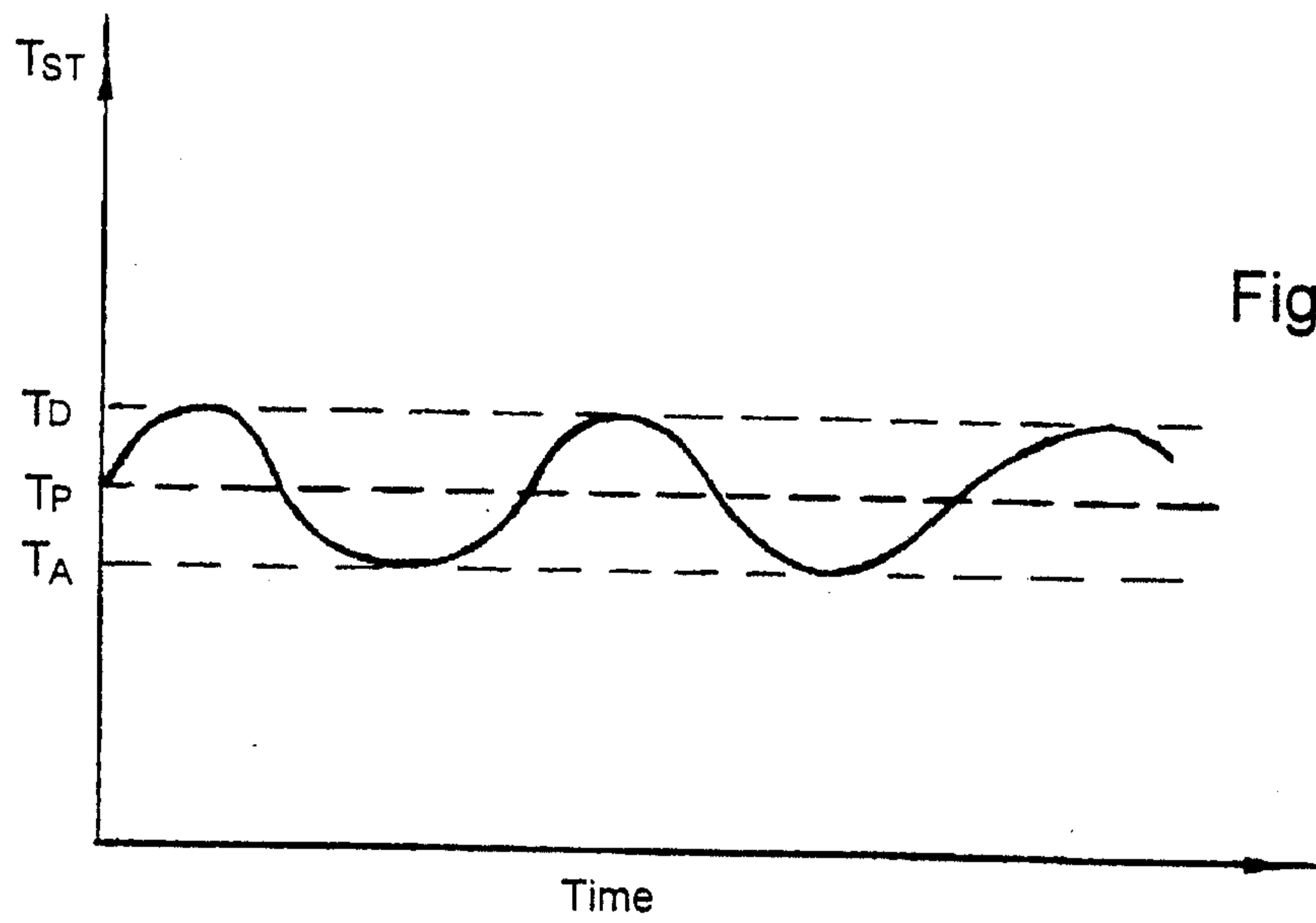


Fig. 1b

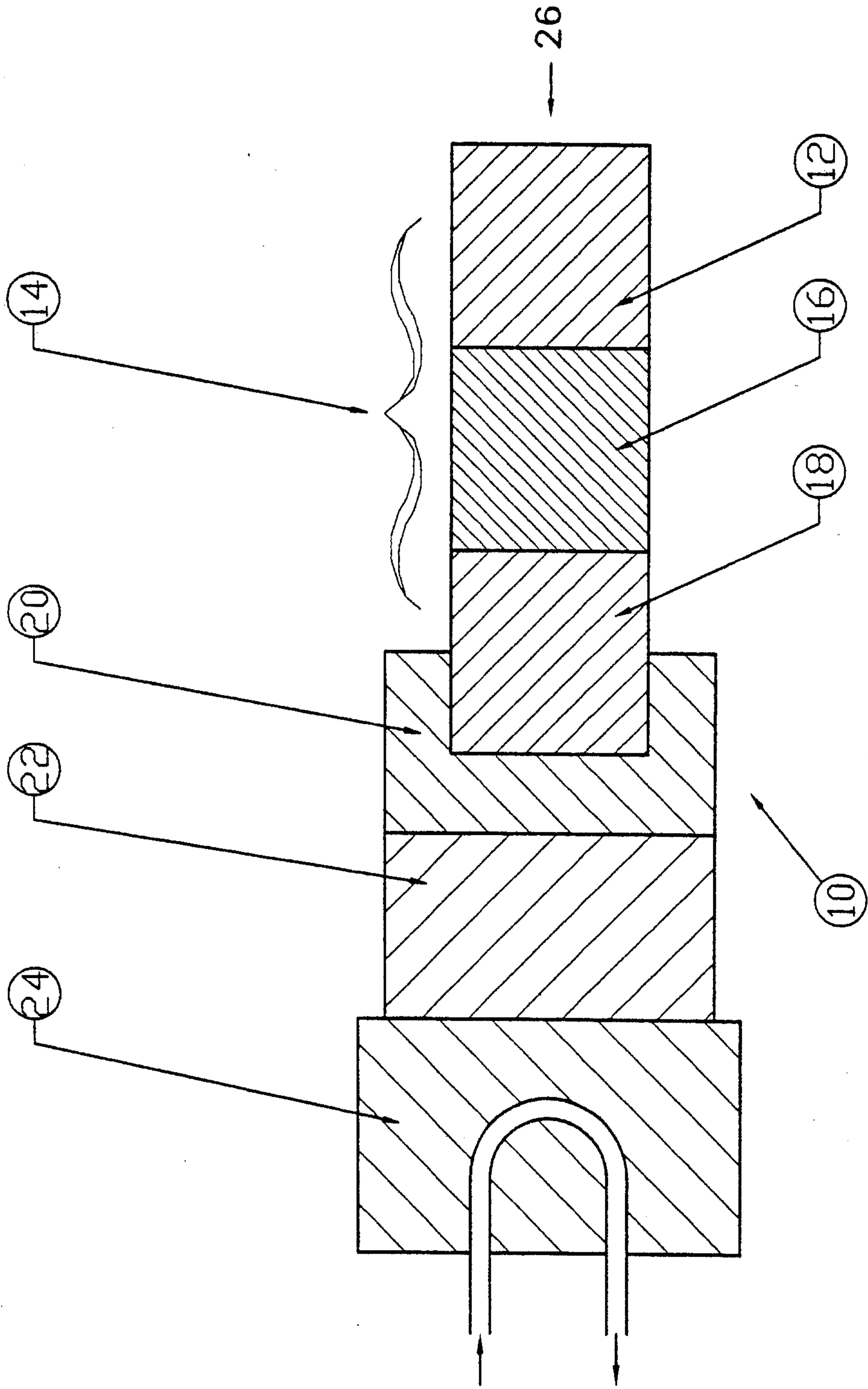


Fig. 2

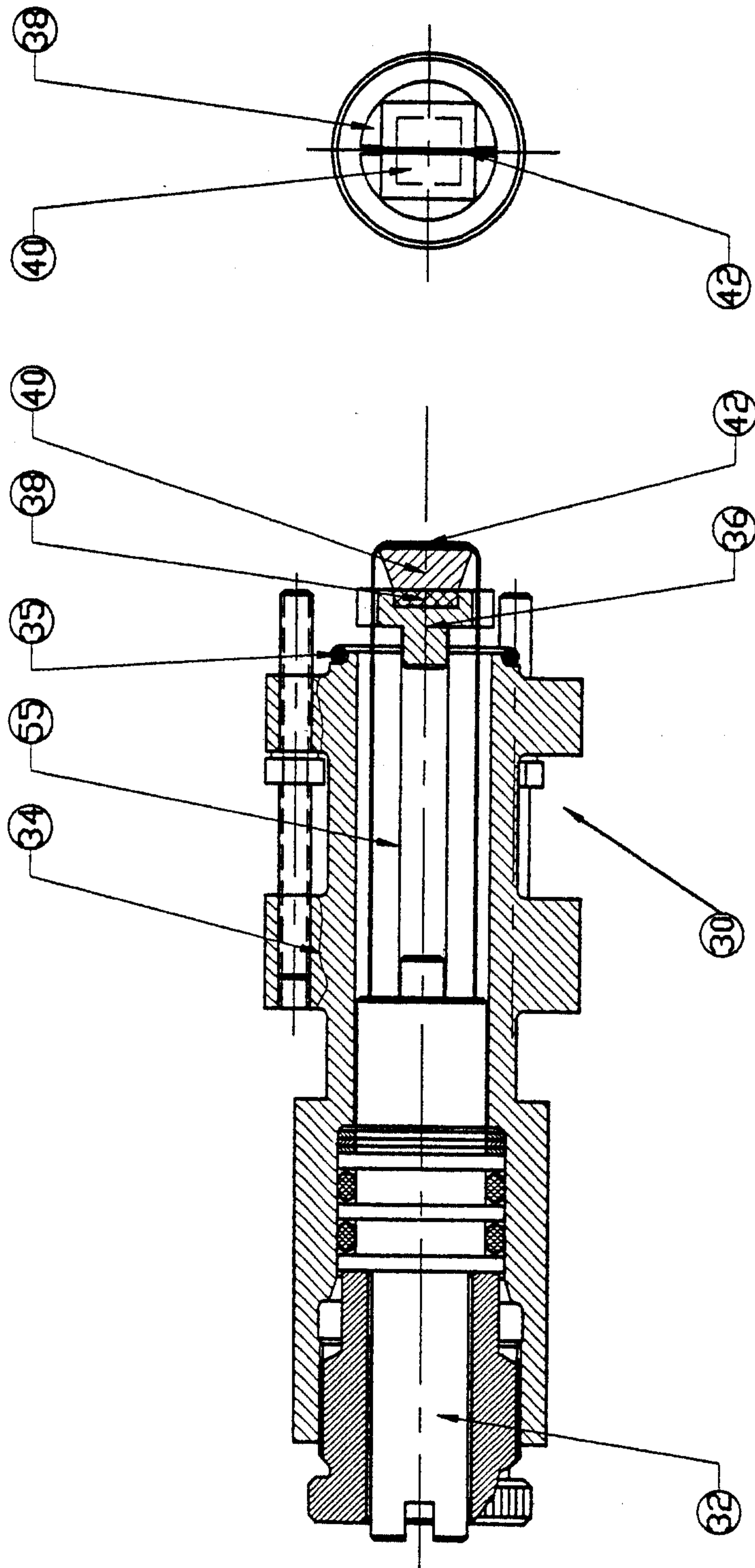


Fig. 3a

Fig. 3b

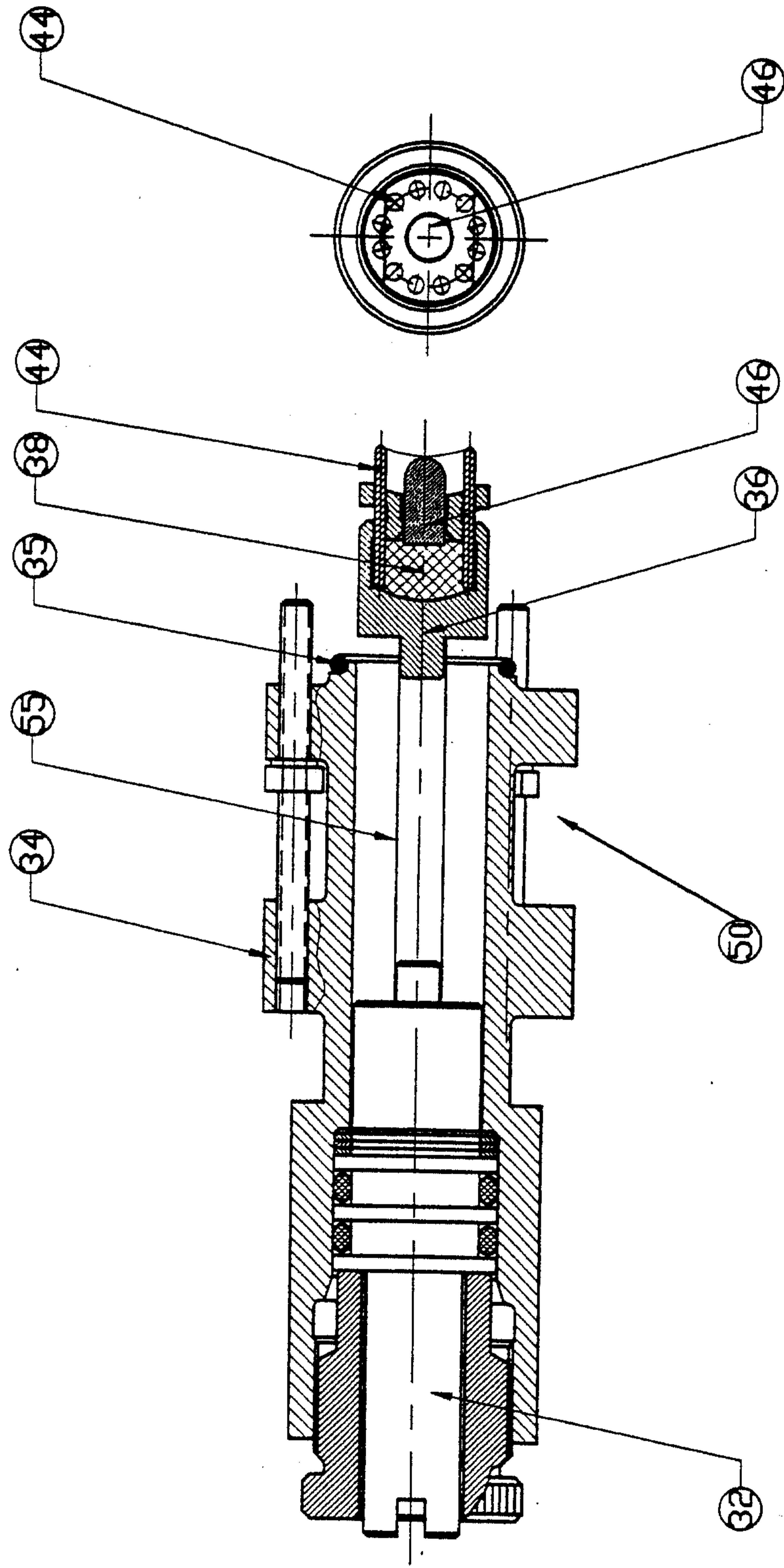
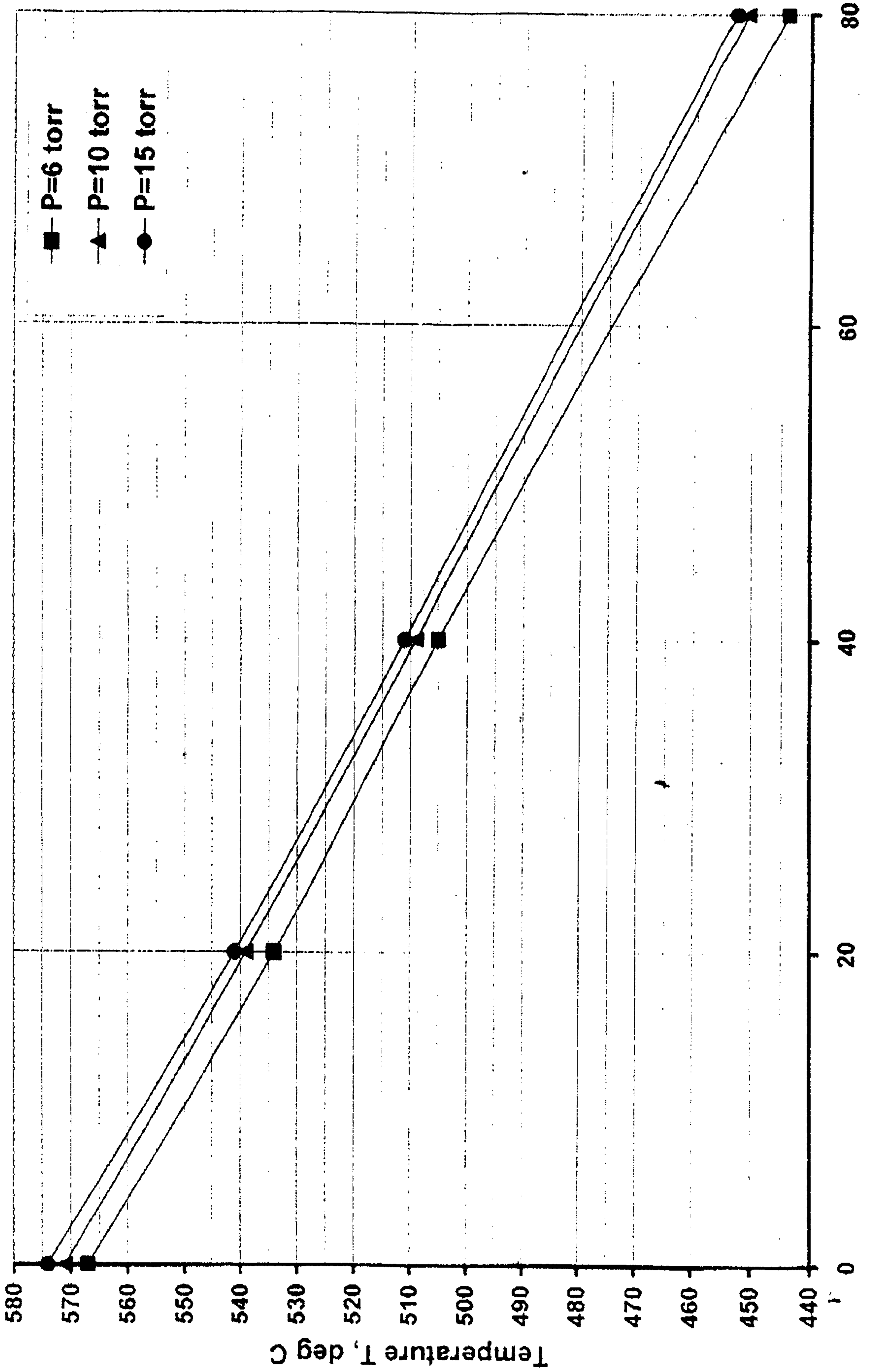


Fig. 4a

Fig. 4b

Temperature of the back butt-end of dental bur vs. Tin concentration in BN/Tin Thermal Compound



Tin concentration in BN/Tin Thermal Compound, weight %

Fig 5.

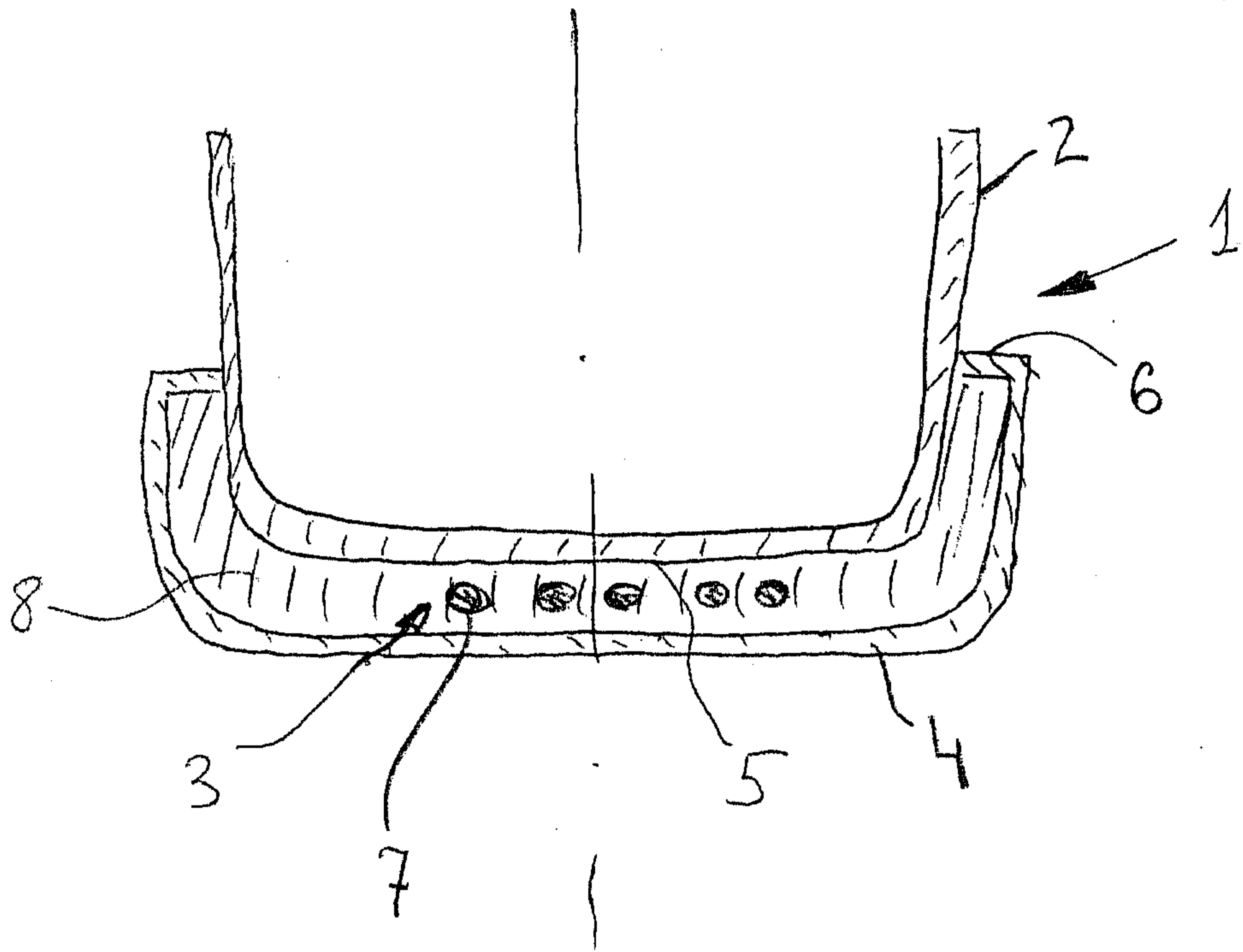


Fig. 6

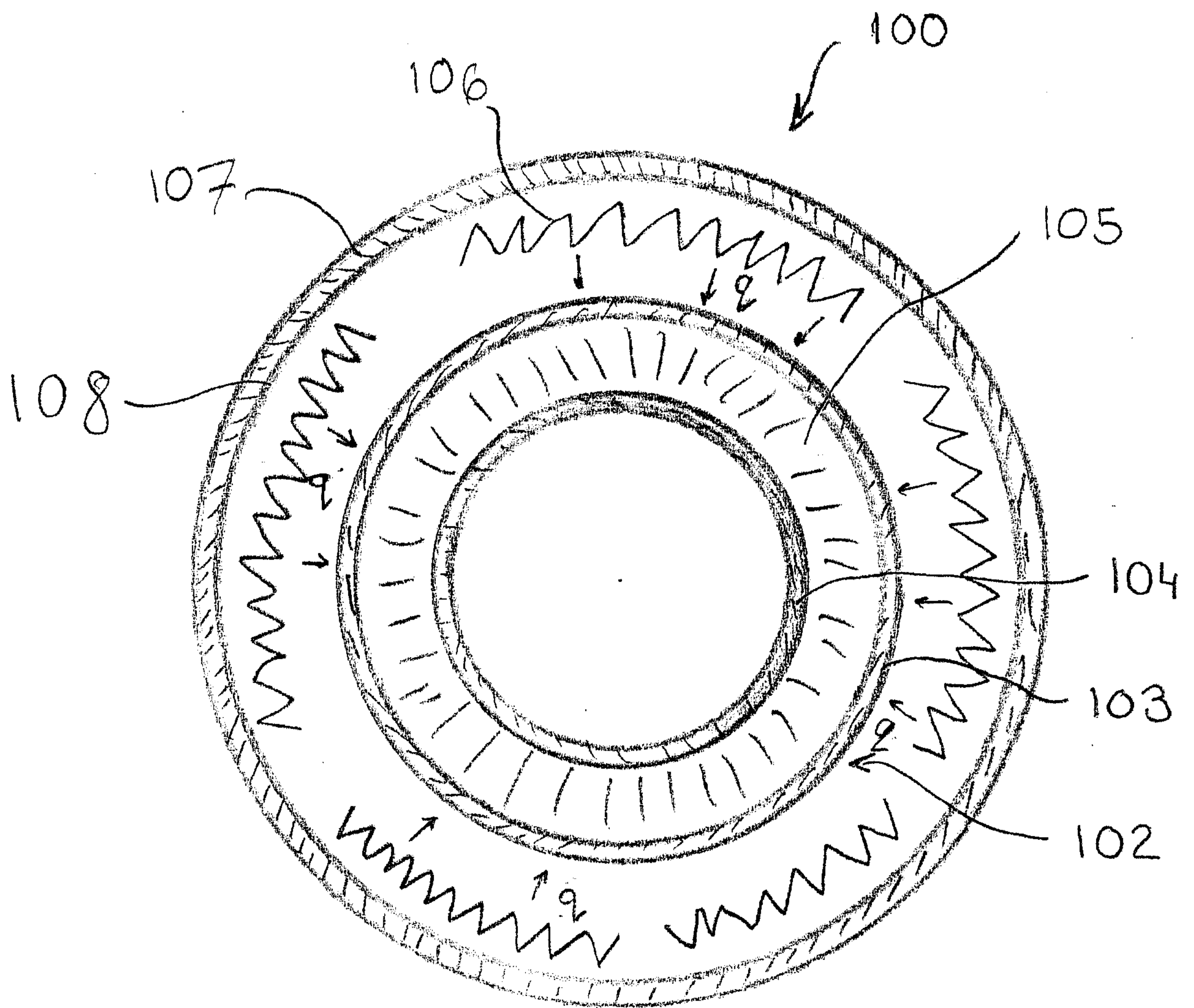


Fig. 7a

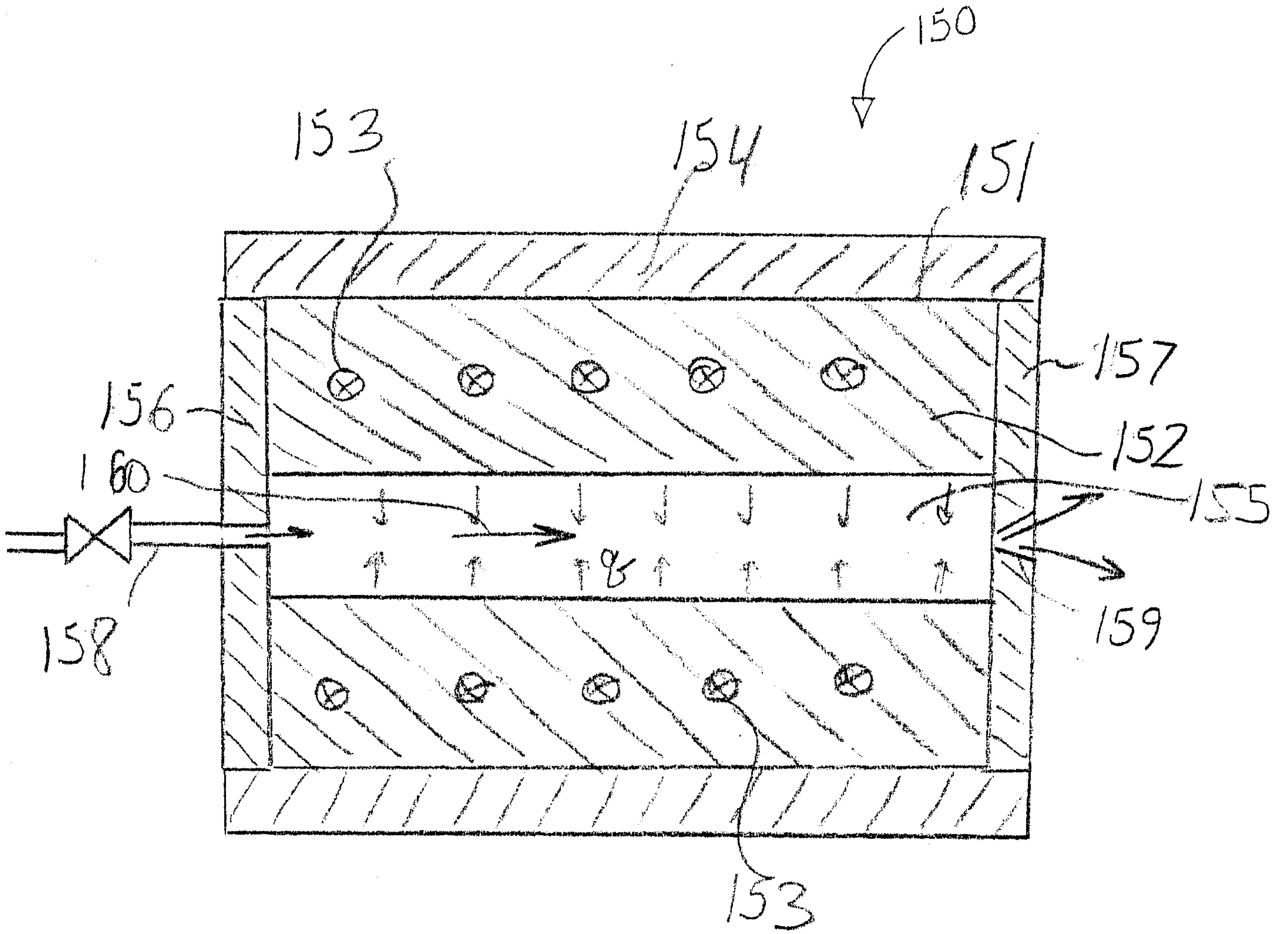


Fig. 76

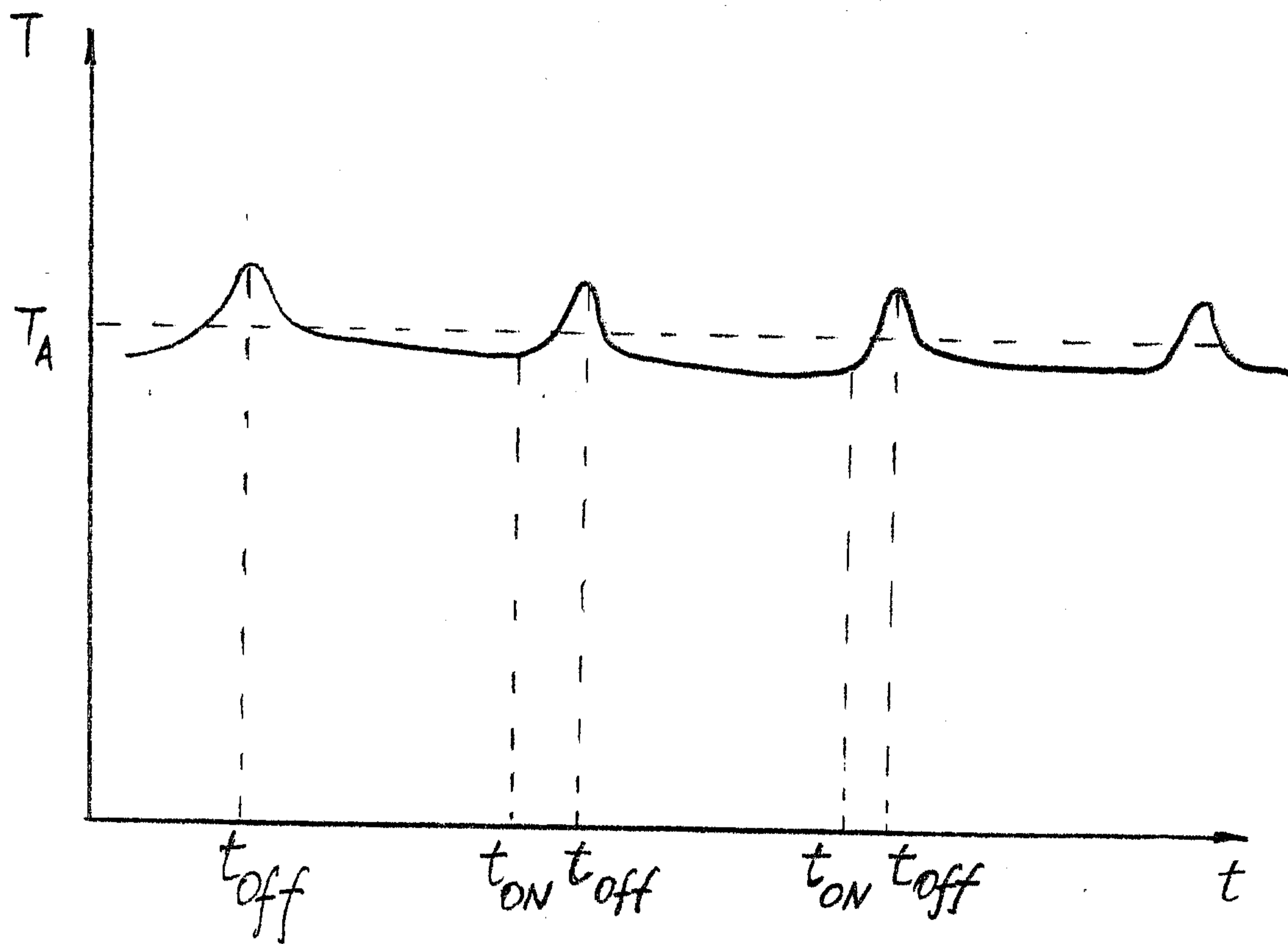


Fig. 8

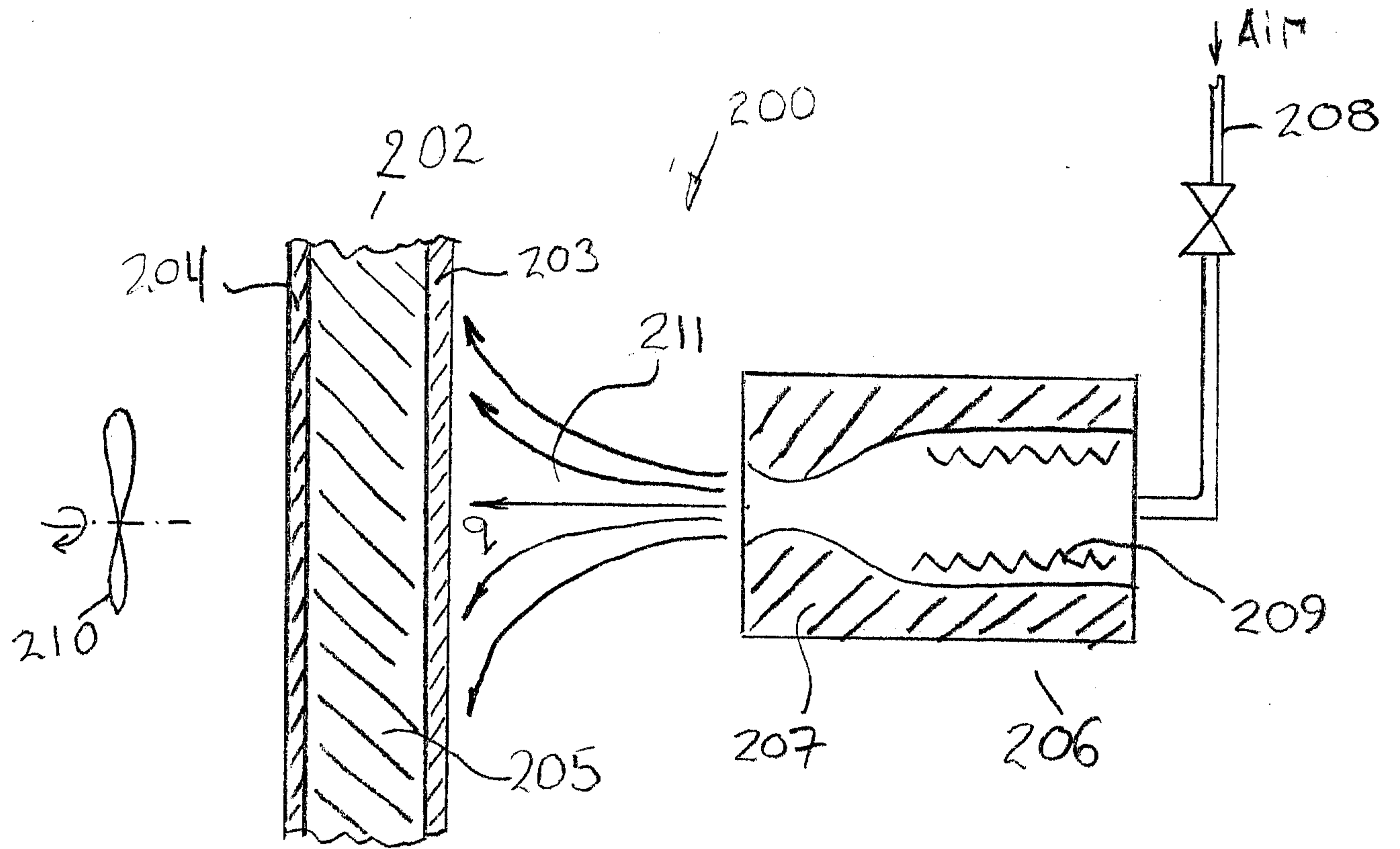


Fig. 9

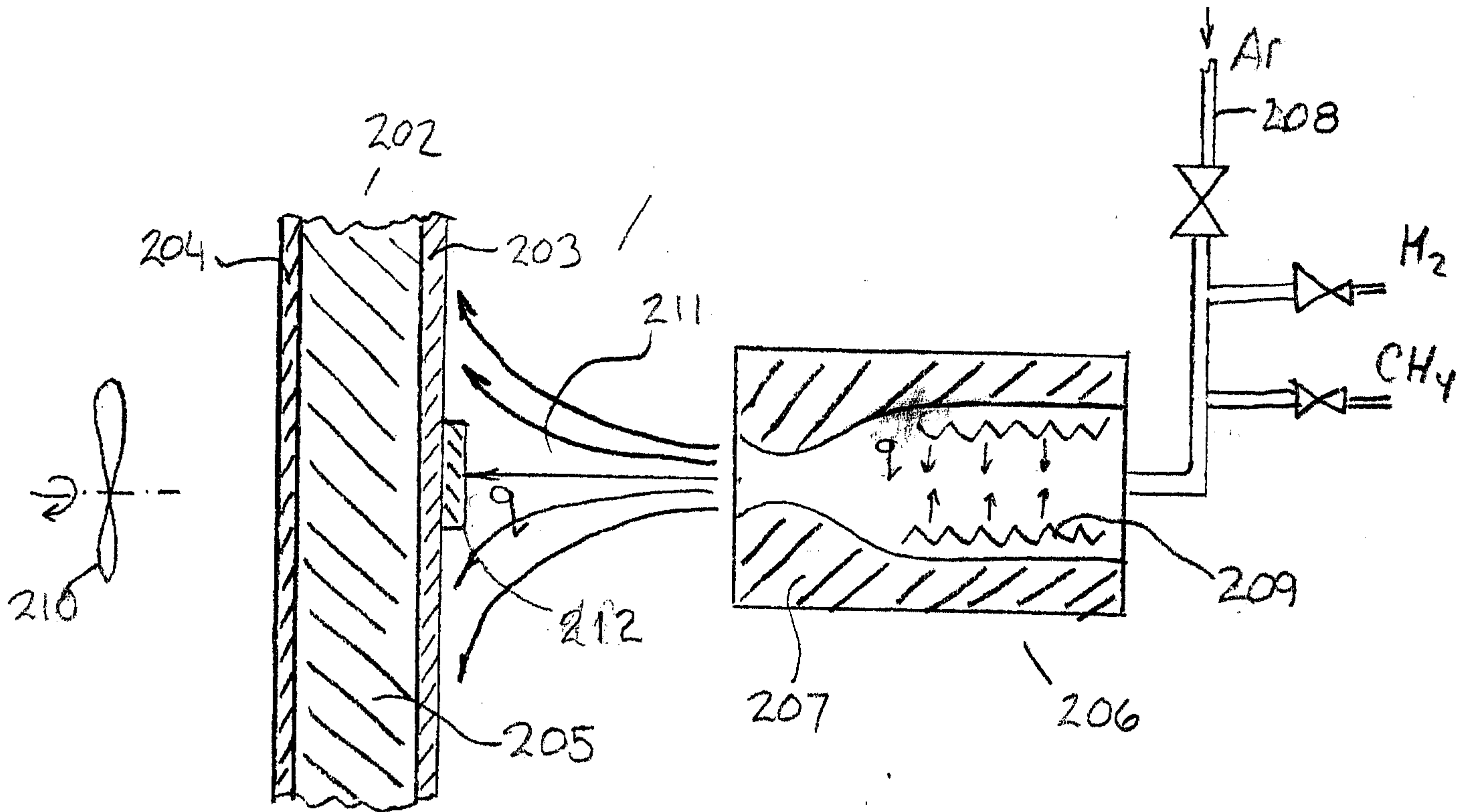


Fig. 10

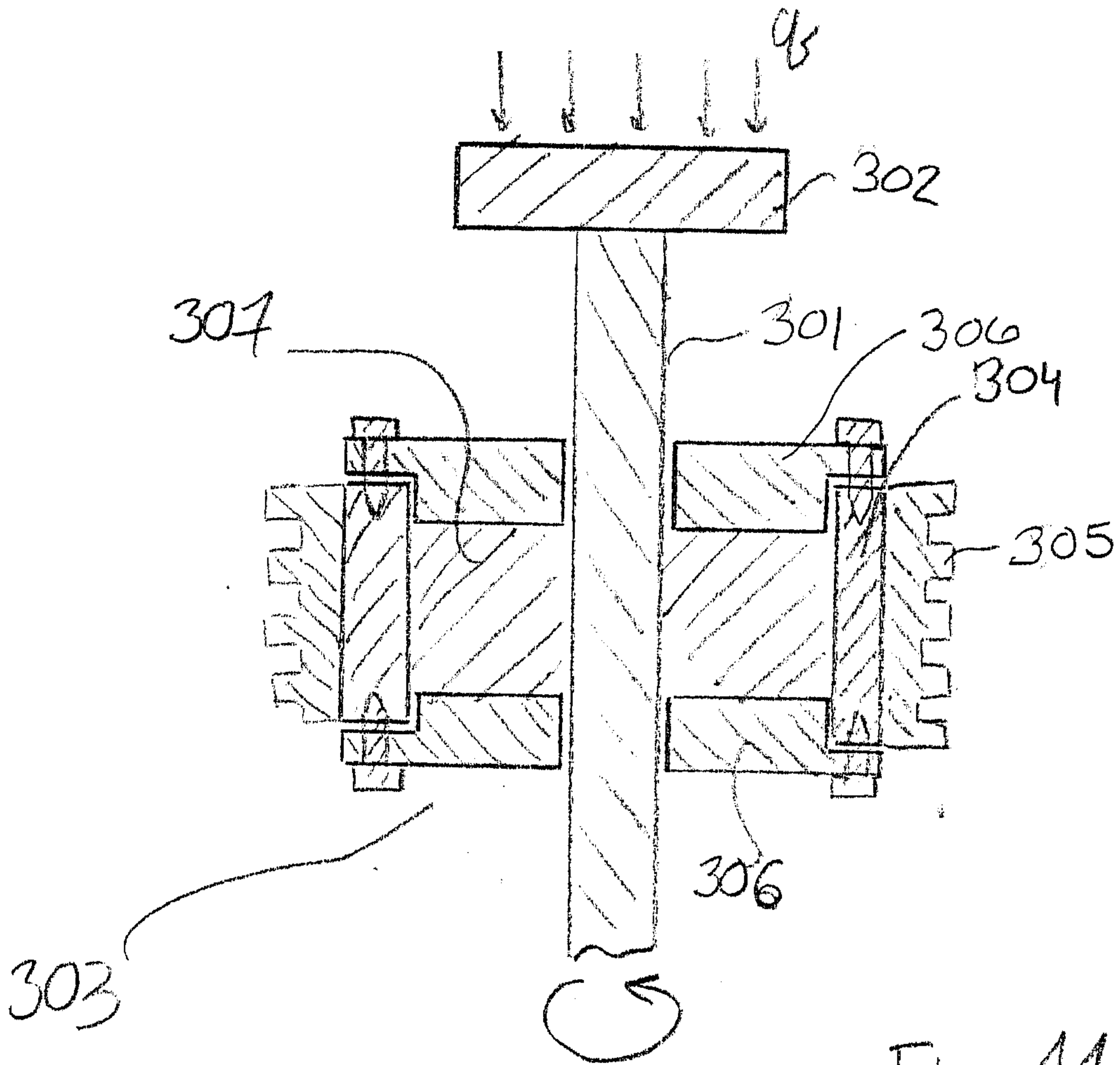


Fig. 11

