PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C30B 15/12, 35/00

A1

(11) International Publication Number: **WO 96/00317**

(43) International Publication Date: 4 January 1996 (04.01.96)

(21) International Application Number: PCT/GB95/01305

(22) International Filing Date: 6 June 1995 (06.06.95)

(30) Priority Data:
9412629.9 23 June 1994 (23.06.94) GB

(71) Applicant *(for all designated States except US)*: THE SECRETARY OF STATE FOR DEFENCE [GB/GB]; Defence Evaluation & Research Agency, DRA Farnborough, Hampshire GU14 6TD (GB).

(72) Inventor; and
(75) Inventor/Applicant *(for US only)*: BESWICK, John, Alfred [GB/GB]; DRA Malvern, St. Andrews Road, Malvern, Worcestershire WR14 3PS (GB).

(74) Agents: BECKHAM, Robert, William et al.; Defence Evaluation & Research Agency, Intellectual Property Dept., R69 Building, DRA Farnborough, Hampshire GU14 6TD (GB).

(81) Designated States: CN, GB, JP, KR, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: IMPROVEMENTS IN CRYSTAL GROWTH

(57) Abstract

Improvements in the growth of homogeneous crystals from a multicomponent melt comprising a double crucible assembly with an injector which affords improved flow of melt from the outer to the inner crucible; guide rods which are external to the outer crucible and which afford locating of the inner crucible with reduced probability of sticking; means for withdrawing the inner crucible after crystal growth is complete and a method of removing trapped gas from the apparatus prior to crystal growth.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	**GB**	United Kingdom	**MR**	Mauritania
AU	Australia	**GE**	Georgia	**MW**	Malawi
BB	Barbados	**GN**	Guinea	**NE**	Niger
BE	Belgium	**GR**	Greece	**NL**	Netherlands
BF	Burkina Faso	**HU**	Hungary	**NO**	Norway
BG	Bulgaria	**IE**	Ireland	**NZ**	New Zealand
BJ	Benin	**IT**	Italy	**PL**	Poland
BR	Brazil	**JP**	Japan	**PT**	Portugal
BY	Belarus	**KE**	Kenya	**RO**	Romania
CA	Canada	**KG**	Kyrgystan	**RU**	Russian Federation
CF	Central African Republic	**KP**	Democratic People's Republic of Korea	**SD**	Sudan
CG	Congo			**SE**	Sweden
CH	Switzerland	**KR**	Republic of Korea	**SI**	Slovenia
CI	Côte d'Ivoire	**KZ**	Kazakhstan	**SK**	Slovakia
CM	Cameroon	**LI**	Liechtenstein	**SN**	Senegal
CN	China	**LK**	Sri Lanka	**TD**	Chad
CS	Czechoslovakia	**LU**	Luxembourg	**TG**	Togo
CZ	Czech Republic	**LV**	Latvia	**TJ**	Tajikistan
DE	Germany	**MC**	Monaco	**TT**	Trinidad and Tobago
DK	Denmark	**MD**	Republic of Moldova	**UA**	Ukraine
ES	Spain	**MG**	Madagascar	**US**	United States of America
FI	Finland	**ML**	Mali	**UZ**	Uzbekistan
FR	France	**MN**	Mongolia	**VN**	Viet Nam
GA	Gabon				

IMPROVEMENTS IN CRYSTAL GROWTH.

This invention relates to a method of growing crystals of uniform composition.

The growth of low defect single crystals has been the subject of considerable research in for example the semiconductor industry. Such crystals are an essential precursor in the fabrication of a vast variety of semiconductor devices.

The Czochralski seed-pulling technique for growing single crystals is well known (eg Z Physik. Chem. (Liebzig) 92, 219 (1918)). By this technique a seed crystal is brought into contact with molten material (melt) to facilitate further crystallisation. The crystal so produced is drawn from the melt as it grows.

However, for an incongruently solidifying melt of more than one component (where the liquidus and solidus temperatures are different) this method does not give rise to uniform composition throughout the crystal. This is because the composition of crystal which crystalises from a given melt is different in composition from that melt (see, for example, S Glasstone, "The Elements of Physical Chemistry" p384, published by Macmillan, 1956). Hence, for a closed system, the composition of the melt, and hence the growing crystal changes as crystallisation proceeds.

In order to produce crystals of uniform composition, the double crucible technique was developed (eg Journal of Applied Physics, 29, no. 8, (1958) pp1241-1244 and US 5,047,112).

Typically, the apparatus of this technique comprises an outer crucible containing melt of the same composition as the crystal to be grown. An inner crucible floats on the melt in the outer crucible and a small channel through the bottom or side wall of the inner crucible allows melt to flow in from the outer crucible.

The crystal is drawn from the melt in the inner crucible (which is replenished from the outer crucible via the channel) and, under equilibrium conditions, has the same composition as the molten material in the outer crucible.

Typically, the respective melting points of the contents of each crucible are different and an essential feature of the double crucible technique (as applied to an incongruently solidifying melt) is that a temperature differential must be maintained between the outer and inner crucible: the temperature at which the crystal is drawn from the melt in the inner crucible is lower than that required to keep the melt in the outer crucible molten.

For a given melt composition, the temperature differential achieved depends, inter alia, on the dimensions of each crucible (including wall and base thickness), the thermal conductivity of the crucible material, and the power and configuration of the heat source used to achieve melting.

One consequence of the difference in melting points between the respective contents of the two crucibles and of the temperature differential maintained between the two crucibles, is that the melt tends to freeze as it passes through the channel to the inner crucible. The resulting blockage is one of the major problems encountered when using the floating crucible technique with incongruently solidifying melts.

The tendency for freezing to block the hole can be reduced by increasing its diameter but this increases the tendency for diffusion of the melt in the inner crucible back into the outer crucible (see for example G R Blackwell, Solid State Electronics 7 105 (1964)). When this occurs, the composition of melt in the outer crucible no longer remains constant and hence the composition of the crystal produced is no longer uniform.

Another feature of the floating crucible technique is that the inner crucible must be maintained concentric with the outer crucible if a symmetrical temperature distribution across the system is to be maintained. If the inner crucible drifts toward the walls of the outer crucible then undesirable localised freezing of the outer melt is likely.

In response to this problem, inner crucibles have been designed which incorporate spacers or fenders to ensure they remain substantially concentric with the outer crucible. However, this design gives rise to another problem, namely that of sticking of the inner crucible. As crystal growth proceeds, the level of melt in the outer crucible falls and the floating inner crucible falls with it. With the incorporation of fenders or spacers on the inner crucible there is an increased tendency for the inner crucible to stick giving rise to uneven crystal growth or, in extreme cases, halting the growth process altogether.

Another disadvantage of the double crucible technique is that, after crystal growth is complete, residual melt may cool and solidify in the double crucible assembly fusing the two crucibles together. This causes many crucibles to be broken or discarded. Ideally, the two crucibles would be separated before cooling and solidification takes place but crystal growth normally takes place at elevated temperatures and the double crucible assembly is typically maintained in an enclosed, inert atmosphere during growth in order to prevent the components of the melt being oxidised or otherwise degraded. Therefore manual separation of the two crucibles before cooling is difficult without exposing the residual melt to the outside atmosphere.

Another problem commonly encountered when using the double crucible technique is that after charging both crucibles with appropriate melt, gas is often trapped in the channel for allowing melt to pass into the inner crucible and surface tension at the melt-gas interface prevents flow of melt from the outer to the inner crucible.

The current invention offers a solution to the above problems by providing means for reducing the drop in temperature experienced by the melt as it passes through the channel to the inner crucible. This means takes the form of an injector which has the additional advantage that it can be removed and replaced if required. The problem of sticking of the inner crucible is reduced by incorporating locating means which are external to the outer crucible and the problem of residual melt solidifying in the crucibles is reduced by including means for withdrawing the inner crucible immediately after crystal growth is complete. Another aspect of the invention comprises a method of removing trapped gas from the channel in the inner crucible in order to facilitate flow of melt from the outer to the inner crucible.

According to this invention, apparatus for growing crystals comprises

a first crucible for containing a supply of molten material,

a second crucible being adapted for floating on the molten material within the first crucible and having means for allowing molten material to enter from the first crucible,

means for heating the contents of the first crucible and

means for drawing a growing crystal from the melt in the second crucible,

characterised in that the means for allowing molten material to enter the first crucible comprises an injector formed from material of higher thermal conductivity than the material used to form the second crucible and configured to provide relatively high thermal contact with the molten material in the first crucible and relatively low thermal contact with the material in the second crucible.

In a preferred embodiment, the injector is removable.

In a further preferred embodiment, a sealant is used to improve the seal between the injector and the inner crucible.

A further preferred embodiment includes locating means, outside the first crucible, for controlling the distance between the walls of the two crucibles.

In a further preferred embodiment the means for drawing the growing crystal comprises a vertically adjustable pull rod linked to the second crucible such that further raising of the pull rod after crystal growth is complete causes the second crucible to be withdrawn from the first crucible.

According to another aspect of this invention, an improvement to the double crucible technique for crystal growth comprises the steps of:-

enclosing the double crucible assembly, including melts contained in the first and second crucibles, in a gas-tight chamber;

reducing the pressure of the chamber to remove trapped gas from the channel in the second crucible and

repressurising the chamber.

The invention will now be described, by example only, with reference to the following figures in which:

figure 1 is a diagram representing equipment of the prior art typically used in the double crucible method of crystal growth;

figure 2 is a part representation of apparatus incorporating the features of the current invention ;

figures 3a and 3b are respectively schematic cross-section and a view from below of a typical injector used in the current invention and

figure 4 is a part representation of an alternative double crucible arrangement incorporating features of the current invention.

Referring to figure 1, a typical double crucible apparatus 1 includes a first (outer) crucible 2 and a second (inner) crucible 3. Crucibles 2 and 3 are formed from an inert material such as quartz, borosilicate glass, boron nitride or vitreous carbon. A narrow channel 4 is included in inner crucible 3.

Material of the composition desired in the finished crystal is placed in the outer crucible 2 and heated by rf induction coil 5 via susceptor 6 to produce outer melt 7.

The inner crucible 3 is placed on the outer melt 7 and typically is initially charged with material which, after heating to form melt 8, will solidify to form crystals of the desired composition.

During the initial stages of the process, gas which is trapped in channel 4 may prevent or inhibit the flow of melt 7 into inner crucible 3.

Spacers 9 maintain the inner crucible 3 substantially concentric with the outer crucible 2.

The floating crucible apparatus typically includes a vertically adjustable and rotatable pull rod 10 to which a seed crystal 11 is secured by mechanical means such as clamping or wire fastening.

The apparatus may include walls defining a chamber 12 which may be filled to a high pressure with an inert gas such as argon. Alternatively, chamber 12 may be evacuated.

Under certain circumstances, the more volatile components of certain melts tend to be depleted by evaporation. This loss can be reduced by means of an encapsulation layer 13 of, for example, B_2O_3 (eg see GB 1,113,069).

During operation, the pull rod 10 is lowered so that seed crystal 11 is brought onto contact with inner melt 8 and crystallisation is facilitated. As the crystal 14 grows it is rotated and drawn up and out of the inner melt 8 by pull rod 10. As the inner melt is depleted by crystallisation, new melt enters through channel 4 and, under equilibrium conditions, the new melt so entering has the same composition as the growing crystal.

Referring to figure 2, some of the features which are common to the prior art have been omitted. In this embodiment crucibles 2 and 3 are formed from quartz. Outer melt 7 enters inner crucible 3 through injector 15.

After melts 7 and 8 have been formed, chamber 12 is evacuated to a pressure sufficiently low to effect removal of trapped gas from channel 4. The vacuum necessary to remove the gas depends on, inter alia, the viscosity of the melts 7 and 8 and the ambient pressure and is typically less than 100 Nm^{-2}.

After the gas has been removed from channel 4 chamber 12 is restored to the conditions under which crystal growth takes place.

Inner crucible 3 is maintained substantially concentric with outer crucible 2 by three equispaced guide rods 16 (two shown), attached to inner crucible 3 and locating in holes 17. In this particular embodiment, locating holes 17 are situated in susceptor 6. However other arrangements, where the means for locating the inner crucible 3 is outside the outer crucible 2, will be apparent to those skilled in the art.

Inner crucible 3 is linked to pull rod 10 via light chains 18 attached to plate 19. Pull rod 10 is free to rotate independently of plate 19 through which it passes. The position of plate 19 along pull rod 10 is maintained by stop 20. The length of the chains 18 is such that, by the time crystal growth is complete, substantially all of the slack has been taken up and further raising of pull rod 10 causes withdrawal of the inner crucible 3 and guide rods 16. Other arrangements, where further raising of pull rod 10 after crystal growth is complete will effect withdrawal of inner crucible 3 from outer crucible 2, will be apparent to those skilled in the art.

Referring to figures 3a and 3b injector 15 is set in the wall or floor of inner crucible 3 and is formed from a material of high conductivity, in this embodiment, graphite. The injector 15 includes a channel 4 and is substantially conical in shape with a flange at one end so that the thermal contact with the outer melt 7 is significantly greater than with the inner melt 8. Thus, the reduction in temperature experienced by the outer melt 7 as it flows through the channel 4 is reduced.

Injector 15 is held in place by quartz rods 22 located in eyes 23. Quartz rods 22 are typically about 2 - 3cm long with a cross-sectional diameter of about 1 - 2mm and at these dimensions exhibit significant flexibility and resilience.

Injector 15 is removable and, as an alternative to the evacuation procedure detailed above for removing trapped gas from channel 4, it may be removed and filled with melt material before assembly of the apparatus.

Other injector configurations, which give rise to a higher thermal contact with the outer melt 7 than with the inner melt 8, will be apparent to those skilled in the art.

The seal between the injector 15 and the wall of the inner crucible 3 may be improved by use of an appropriate sealant 24, for example graphite paper.

Referring to figure 4, when pull rod 10 is raised to a predetermined height (as shown) hooks 25, which are connected to pull rod 10 via plate 19, engage with ring 26 which is attached to guide rods 16. Thus, further raising of pull rod 10 causes inner crucible 3 to be raised. Pull rod 10 is free to rotate independently of plate 19 through which it passes. The position of plate 19 along pull rod 10 is maintained by stop 20. This arrangement has the additional advantage that, during operation, the inner crucible 3 may be rotated independently of the link to plate 19.

CLAIMS.

1. Apparatus for growing crystals comprising:-

a first crucible for containing a supply of molten material,

a second crucible being adapted for floating on the molten material within the first crucible and having means for allowing molten material to enter from the first crucible,

means for heating the contents of the first crucible,

means for drawing a growing crystal from the melt in the second crucible,

characterised in that the means for allowing molten material to enter the first crucible comprises an injector formed from material of higher thermal conductivity than the material used to form the second crucible and configured to provide relatively high thermal contact with the molten material in the first crucible and relatively low thermal contact with the material in the second crucible.

2. The apparatus of claim 1 where the injector is removable.

3. The apparatus of claim 1 where a sealant is used to improve the seal between the injector and the inner crucible.

4. The apparatus of claim 1 and further including locating means, outside the first crucible, for controlling the distance between the walls of the two crucibles.

5. The apparatus of claim 1 where the means for drawing a growing crystal comprises a vertically adjustable pull rod linked to the second crucible such that further raising of the pull rod after crystal growth is complete causes the second crucible to be withdrawn from the first crucible.

6. A method of growing a crystal using the double crucible technique for crystal growth and including the steps of:-

enclosing the double crucible assembly, including melts contained in the first and second crucibles, in a gas-tight chamber;

reducing the pressure of the chamber to remove trapped gas from the channel in the second crucible and

repressurising the chamber.

Fig.1.
Prior Art

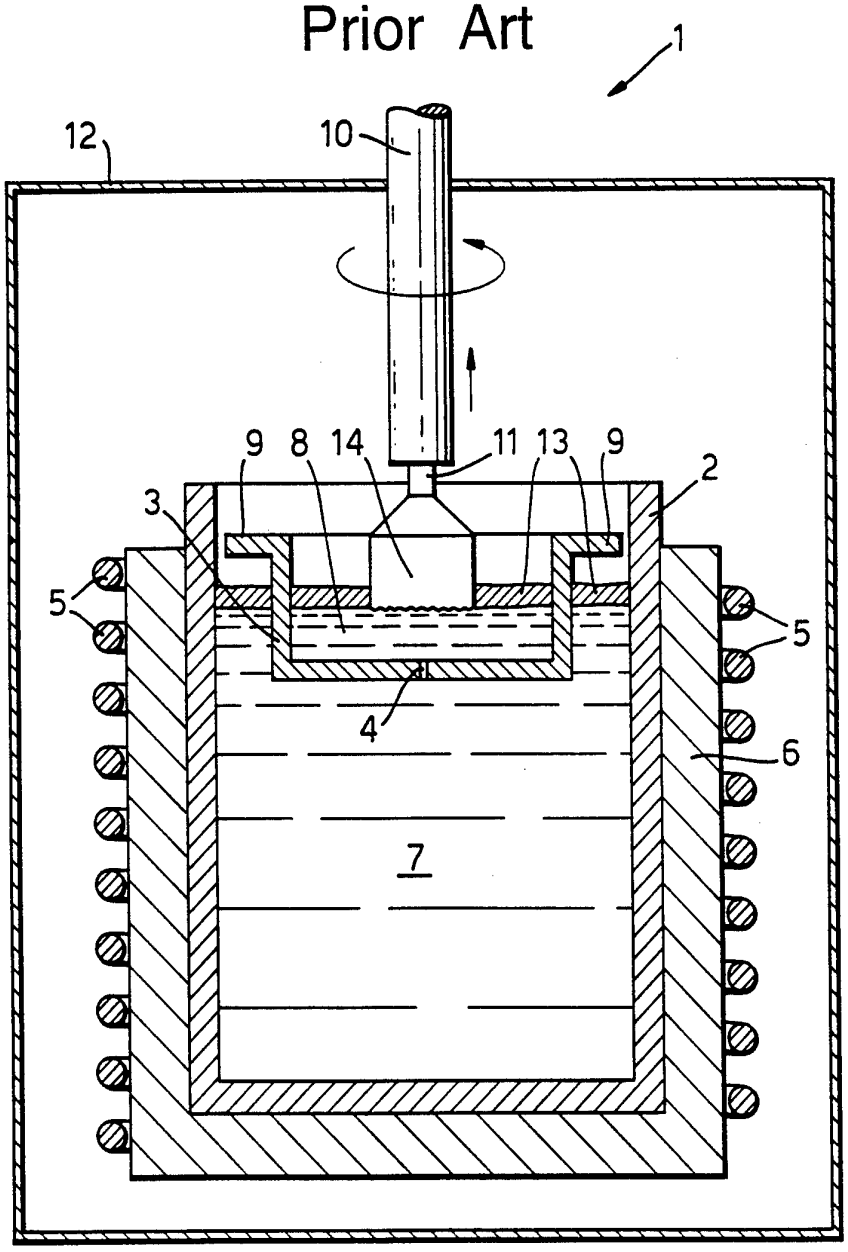


Fig.2.

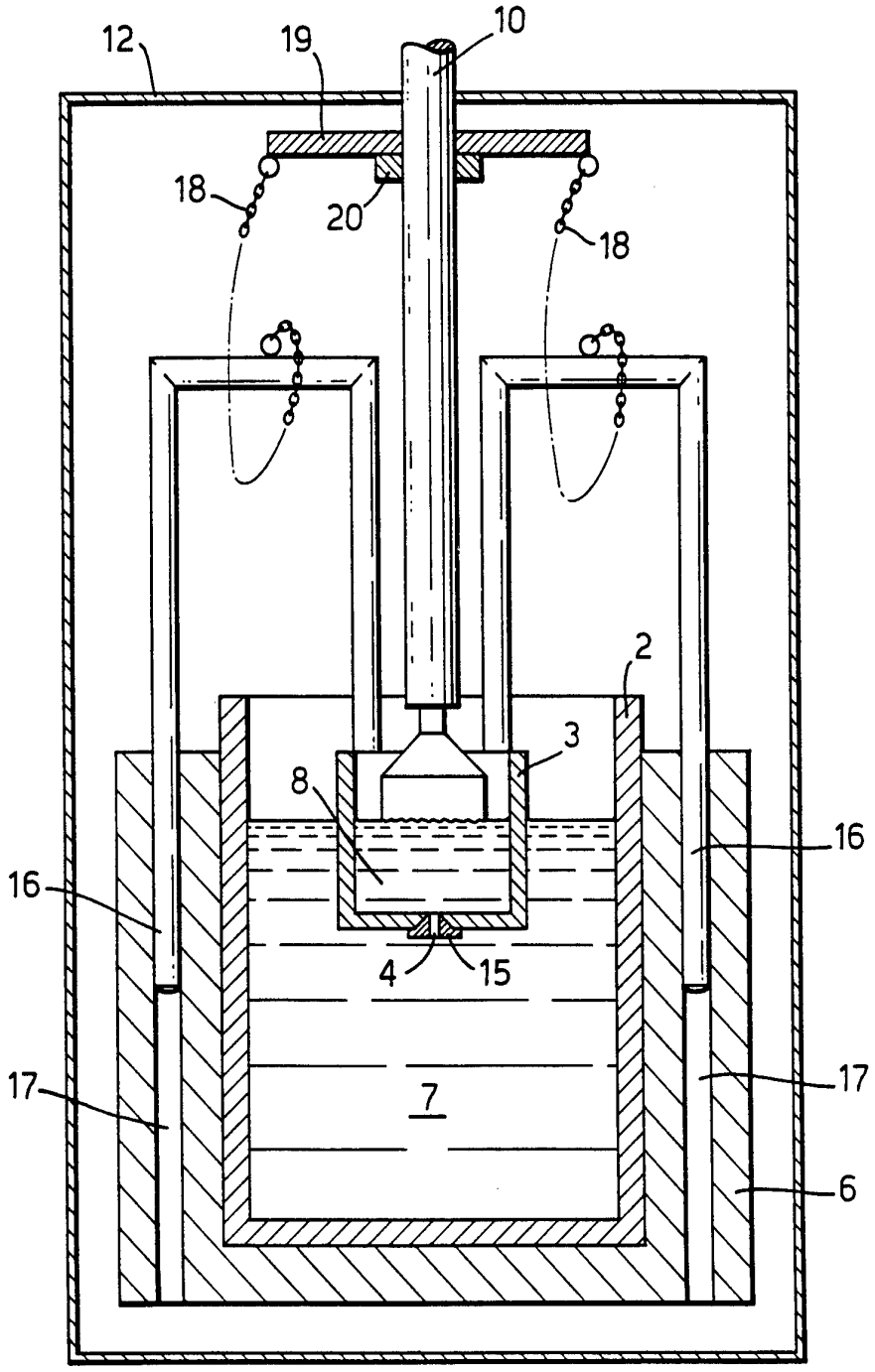


Fig.3a.

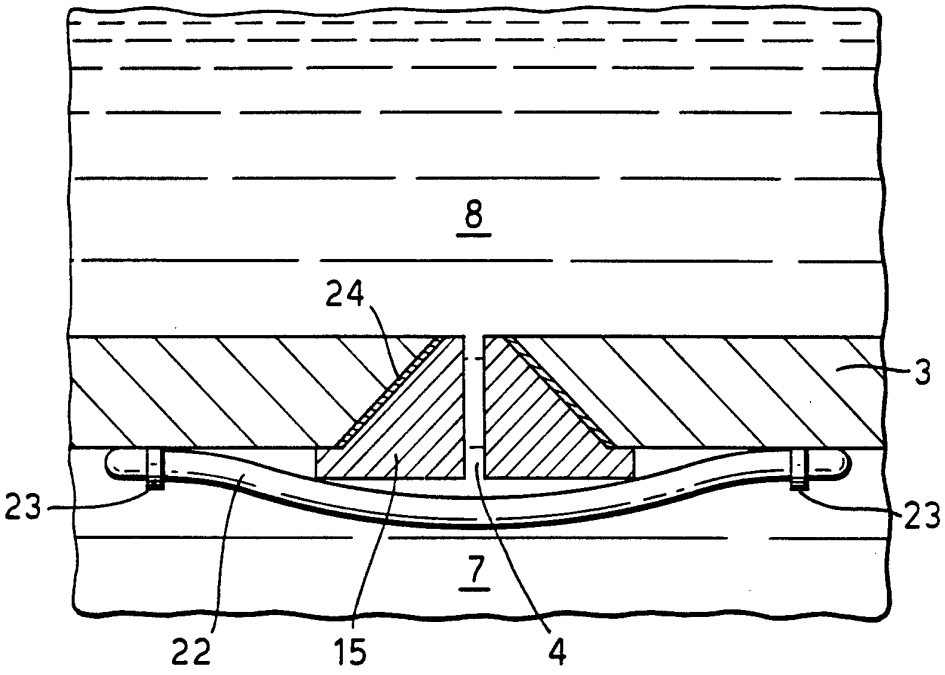


Fig.3b.

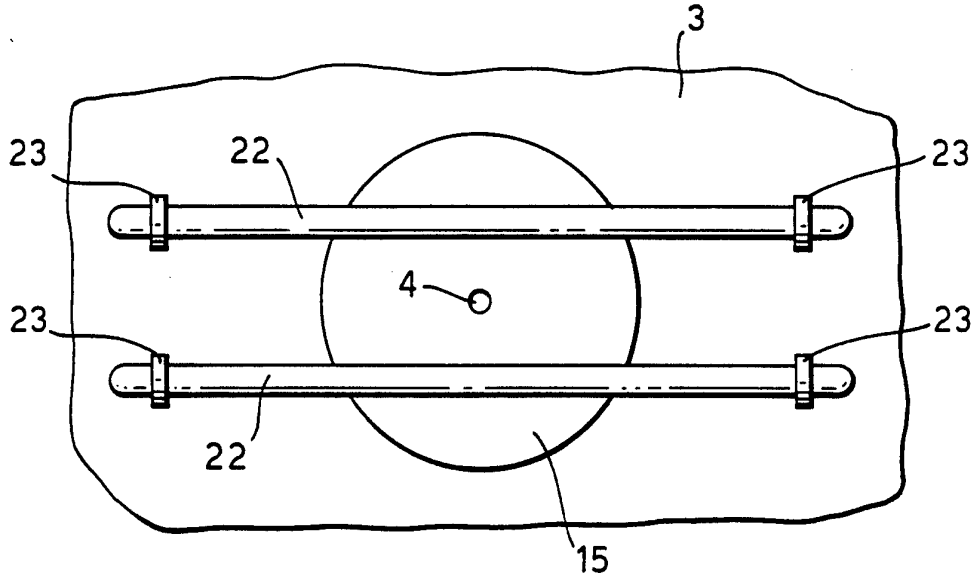
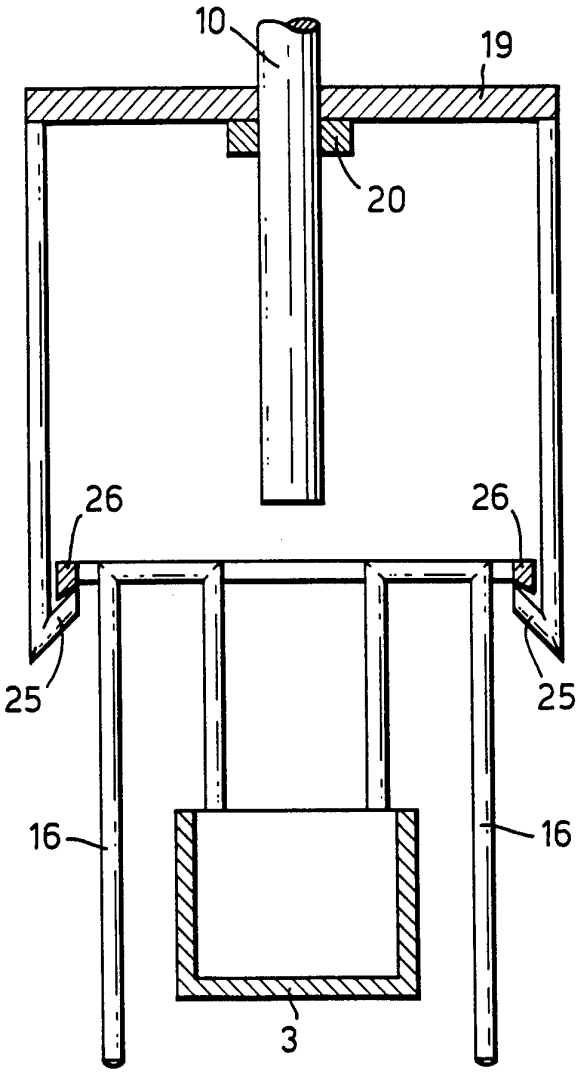


Fig.4.



INTERNATIONAL SEARCH REPORT

Internati. Application No PCT/GB 95/01305

A. CLASSIFICATION OF SUBJECT MATTER
C 30 B 15/12,C 30 B 35/00

According to International Patent Classification (IPC) or to both national classification and IPC 6

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C 30 B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP, A, 0 525 765 (MITSUBISHI MATERIALS CORP.) 03 February 1993 (03.02.93), claims 1,6; fig. 1. --	1-6
A	EP, A, 0 364 899 (MITSUBISHI METAL CORP.) 25 April 1990 (25.04.90), claims 1,4; fig. 6. --	1-6
A	EP, A, 0 226 794 (SUMITOMO ELECTRIC INDUSTRIES) 01 July 1987 (01.07.87), claims 1-5; fig. 1. --	1-6
A	EP, A, 0 321 576 (MITSUI MINING COMPANY) 28 June 1989 (28.06.89),	1-6

[X] Further documents are listed in the continuation of box C. [ ] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
12 September 1995	6. 10. 95

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	BRUS e.h.

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Interna l Application No
PCT/GB 95/01305

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	claim.	

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

ANHANG — ANNEX — ANNEXE

zum internationalen Recherchenbericht über die internationale Patentanmeldung Nr. — to the International Search Report to the International Patent Application No. — au rapport de recherche international relatif à la demande de brevet international n°

PCT/GB 95/01305 SAE 111129

In diesem Anhang sind die Mitglieder der Patentfamilien der im obengenannten internationalen Recherchenbericht angeführten Patentdokumente angegeben. Diese Angaben dienen nur zur Unterrichtung und erfolgen ohne Gewähr.

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The Office is in no way liable for these particulars which are given merely for the purpose of information.

La présénte annexe indique les membres de la famille de brevets relatifs aux documents de brevets cités dans le rapport de recherche international visée ci-dessus. Les reseignements fournis sont donnés à titre indicatif et n'engagent pas la responsibilité de l'Office.

Im Recherchenbericht angeführtes Patentdokument Patent document cited in search report Document de brevet cité dans le rapport de recherche	Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
EP A1 525765	03-02-93	DE C0 69201693	20-04-95
		DE T2 69201693	07-09-95
		EP B1 525765	15-03-95
		JP A2 5085880	06-04-93
		US A 5306474	26-04-94
EP A1 364899	25-04-90	DE C0 68916157	21-07-94
		DE T2 68916157	24-11-94
		EP B1 364899	15-06-94
		JP A2 2107587	19-04-90
		US A 5196173	23-03-93
EP A1 226794	01-07-87	CA A1 1317202	04-05-93
		DE C0 3674744	08-11-90
		EP B1 226794	03-10-90
		JP A2 62128999	11-06-87
		US A 5021118	04-06-91
EP A1 321576	28-06-89	WO A1 8810329	29-12-88
		DE C0 3876225	07-01-93
		DE T2 3876225	17-06-93
		EP B1 321576	25-11-92
		JP A2 63310786	19-12-88
		US A 5312506	17-05-94