



Europäisches Patentamt
European Patent Office
Office européen des brevets



Publication number: **0 530 968 A1**

EUROPEAN PATENT APPLICATION

Application number: **92306862.1**

Int. Cl.⁵: **C22C 1/02, C22C 14/00, C22C 21/00, B22D 27/04**

Date of filing: **28.07.92**

Priority: **29.08.91 US 738759**

Inventor: **Huang, Shyh-Chin**
6 Starboard Way
Latham, New York 12110(US)

Date of publication of application:
10.03.93 Bulletin 93/10

Designated Contracting States:
DE FR GB IT

Representative: **Pratt, Richard Wilson et al**
London Patent Operation G.E. Technical
Services Co. Inc. Essex House 12/13 Essex
Street
London WC2R 3AA (GB)

Applicant: **GENERAL ELECTRIC COMPANY**
1 River Road
Schenectady, NY 12345(US)

Method for directional solidification casting of a titanium aluminide.

A method for directional solidified vacuum or protective atmosphere casting of gamma titanium aluminide alloys in a mold comprised of a chill and a sidewall means extending from the chill to form a cavity for holding a molten metal, the method comprising, forming a melt of the gamma titanium aluminide alloy in the cavity, the melt being comprised of a metal from the group consisting of niobium, tantalum, tungsten, and molybdenum in an effective amount to reduce oxygen pickup in the melt, the sidewall means having at least an inner liner of a calcia refractory facing the melt. The melt is heated in a thermal gradient sufficient to cause directional solidification of the melt from the chill.

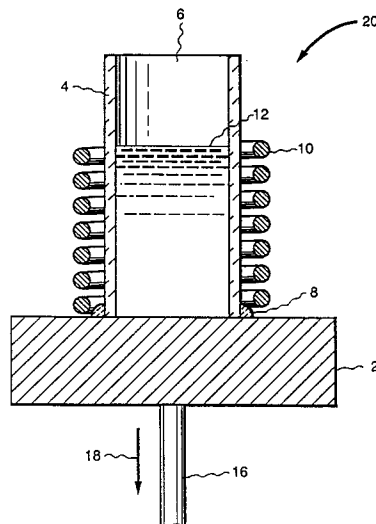


FIG. 1

EP 0 530 968 A1

This invention is related to a method for directional solidification casting of a titanium aluminide alloy.

Most metal castings are formed into components subjected to isotropic stress fields, but there are applications where the stress applied to a component formed from a casting is primarily unidirectional along a single axis. For example, gas turbine engine blades experience high stresses along the major axis of the blade, as well as high temperatures. Because grain boundaries are weaker than grains at high temperature, improved properties are found by aligning the grains parallel to the axis of principal stress to minimize the effect of grain boundaries on the properties. Casting practices have been developed that align grains in a columnar structure along such axis of primary stress, and enhance the properties. One well known method is directional solidification. Specialized furnaces are used, and mold design is quite different than that used for conventional investment castings.

In columnar grain structures, the primary dendrites are aligned, as are the grain boundaries. To obtain a directionally solidified structure, it is necessary to cause the dendrites to grow from one end of the casting to the other. This is accomplished by removing the bulk of the heat from one end of the casting. For example, a strong thermal gradient is established in the temperature zone between the liquidus and solidus temperatures of the alloy, and is passed from one end of the casting to the other at a rate that maintains the steady growth of the dendrites. An effective way to control heat flow is in a mold assembly having thin refractory sidewalls and a metal chill, usually water cooled, at the lower end of the mold. The sidewalls of the mold assembly are heated above the liquidus temperature of the alloy by a mold heating device such as an induction heater. Molten metal is poured into the mold, and after a pause of a few minutes to allow the grains to nucleate and begin to grow on the chill, the mold is withdrawn at a controlled rate from the mold heating device.

Considerable effort has been devoted to providing refractory materials suitable for casting titanium and titanium aluminide alloys. Shape casting of titanium was first demonstrated in the United States in 1954 at the U.S. Bureau of Mines using machined high-density graphite molds. Later, a rammed graphite mold process was developed using powdered graphite mixed with organic binders. Investment casting methods developed in the mid-1960s required the development of ceramic slurry materials with minimum reaction to the extremely reactive molten titanium. In such investment casting methods, a face coat made with special refractory oxides and appropriate binders resistant to reaction with molten titanium is applied to a wax pattern, and more traditional refractory systems are used to backup the face coatings and add strength to the mold.

Regardless of the face coat composition, some reaction between molten metal and mold occurs from titanium reduction of the ceramic oxides. An oxygen-rich surface is formed on the casting that stabilizes the alpha phase in titanium forming a distinct "alpha case" layer on the cast surface. The brittle alpha case layer can be removed by chemical milling. Diffusion of reaction products into the surface of the casting is dependent on the time the titanium is at a temperature sufficient to react with the mold. The depth of surface contamination must be taken into consideration in the initial wax pattern tool design. Hence, the wax pattern and casting are made slightly oversized, and final dimensions are achieved through careful chemical milling. Metal superheat, mold temperature and thermal conductivity, and rapid removal of heat after casting are other factors in to control for producing a satisfactory casting.

Examples of face coatings and refractory materials that have been developed for casting titanium and titanium alloys are given in U.S. Patent 4,740,246. Briefly described, some of the face coating compositions are; a silica binder prepared either from ethyl silicate, aqueous colloidal silica or the like, is used to bond boron oxide; a zirconia refractory bonded by zirconium acetate; a stabilized zirconia refractory bonded by colloidal silica, and a zirconia sol binder for a refractory material selected from fused yttrium oxide, a fused mixture of yttrium oxide and zirconium oxide, a fused blend of zirconium oxide and yttrium oxide with an oxide of rare earth elements of the periodic table elements with an atomic number of 57-71, a fused blend of zirconium oxide with an oxide of the same rare earth elements, and a fused blend of yttrium oxide with an oxide of the same rare earth elements.

The difficulty in providing mold materials or face coatings having minimized reaction with molten titanium is further exacerbated for forming directionally solidified castings. The long contact time of molten metal with the mold to allow directional solidification, the high temperatures required for casting titanium alloys, and the reactive metal titanium can produce severe metal-mold reactions that must be minimized in order to produce an acceptable casting.

The titanium alloys of interest for casting in the method of this invention are the gamma titanium aluminide based alloys. Gamma titanium aluminides are well known being characterized by a tetragonal crystal structure, and are comprised of about 48 to 58 atom percent aluminum. Gamma titanium aluminide alloys comprised of a minor amount of alpha-2 phase are comprised of as low as 40 atom percent aluminum. Additional elements, for example, chromium, vanadium, niobium, tantalum, silicon, and gallium

have been added to gamma titanium aluminide alloys as shown for example in U.S. Patents 3,203,794; 4,294,615; 4,661,316; 4,857,268; 4,842,820; 4,842,817; 4,836,983; 4,879,092; 4,902,474; 4,897,127; 4,923,534; 4,916,028; incorporated herein by reference. The low ductility of the gamma titanium aluminides at room temperature has been the major limitation to forming components of the alloys. It is well known that oxygen is an interstitial contaminant in gamma titanium aluminides that contributes to the room temperature brittleness of the alloy.

In "Influence of Growth Rate on Microstructure and Tensile Properties of Directionally Solidified TiAl Alloys," M. Takeyama, T. Hirano, T. Tsujimoto, Proceedings of International Symposium on Intermetallic Compounds - Structure and Mechanical Properties, The Japan Institute of Metals, 1991, pp. 507-511, it was disclosed that a gamma titanium aluminide alloy was directionally solidified by the floating zone method. Bar ingots of three gamma titanium aluminide alloys comprised of 48 atomic percent aluminum, 50 atomic percent aluminum, and 52 atomic percent aluminum were unidirectionally solidified by an optically heated floating zone. In the floating zone method, a small zone of the bar is initially melted and moved slowly through the bar. The molten zone is held in place by surface tension forces so that a crucible is unnecessary for holding the casting as it directionally solidifies. The floating zone method of forming directionally solidified castings is comparatively slow, energy intensive, and limited in the shapes that can be formed.

It is an object of this invention to provide a method for directional solidification casting of a gamma titanium aluminide alloy in a mold, while minimizing reaction with the mold and oxygen pickup in the casting.

Brief Description of the Invention

The method of this invention provides for directional solidification vacuum or protective atmosphere casting of gamma titanium aluminide alloys. The directional solidification casting is performed in a mold comprised of a chill and a sidewall means extending from the chill to form a cavity for holding a molten metal. A melt of the gamma titanium aluminide alloy comprised of an effective amount of a metal from the group consisting of niobium, tantalum, tungsten, and molybdenum to reduce oxygen pickup in the melt is formed in the cavity, the sidewall means having at least an inner liner of a calcia refractory facing the melt. The melt is heated in a thermal gradient sufficient to cause directional solidification of the melt from the chill. Preferably, the melt is comprised of about 2 to 12 atom percent niobium, and most preferably about 4 to 8 atom percent niobium.

Detailed Description of the Invention

The method of this invention can be used for directional solidification casting of the gamma titanium aluminide alloys. The casting is performed in a vacuum or protective atmosphere that does not react with the molten metal such as argon or helium. In directional solidification casting, a melt is formed in a mold and heated in a thermal gradient to form a directionally solidified crystal structure of columnar grains growing from the surface of a chill in the mold. As a result, the molten portions of the casting are exposed to the mold sidewalls for an extended period of time during which the highly reactive titanium aluminide alloy melt can react with the sidewalls and pickup contaminants such as oxygen. It has been discovered that oxygen pickup during directional solidification casting is reduced when the melt is comprised of an effective amount of a metal from the group consisting of niobium, tantalum, tungsten, and molybdenum to reduce oxygen pickup in the melt, and the mold sidewalls are formed from a calcia refractory. It is well known that the toughness and ductility of gamma titanium aluminides is adversely reduced by oxygen pickup in the melt.

The method of this invention is further shown by making reference to FIG. 1. FIG. 1 is a cross-section of a directional solidification casting assembly 20. Casting assembly 20 is comprised of a chill 2, a cylindrical sidewall 4, and a heating means 10. The casting assembly 20 is located in a vessel, not shown, of conventional construction suitable for containing a vacuum or protective atmosphere. Chill 2 is a metal body capable of solidifying molten titanium or titanium alloys without reacting with the molten metal. A suitable chill 2 is comprised of molybdenum or copper that is water cooled by conventional means not shown. Sidewall 4 is generally cylindrical and extends from chill 2 to form a cylindrical cavity 6 for holding molten metal 12. Preferably, sidewall 4 is sealed against chill 2 by a ceramic seal 8, of conventional material known in the art for forming a high temperature seal of ceramic to metal.

A suitable ceramic seal 8 can be formed by pouring a ceramic slurry comprised of alumina powder in a binder comprised of about 8.3 weight percent K₂O, about 20.8 weight percent silica, and about 70.9 weight

percent water where sidewall 4 contacts chill 2. The ceramic slurry is dried and baked at about 400° C to remove the liquid. Sidewall 4 is formed to have at least an inner liner of a calcia refractory adjacent the molten metal 12. A suitable calcia refractory is comprised of calcia and may contain other ceramics that do not react with molten titanium or titanium alloys. For example, a suitable calcia refractory is comprised of calcia and calcium fluoride, available from Calceed Co., Ltd., Japan. Preferably, sidewall 4 is formed from a high-purity calcia, for example, described in U.S. Patent 4,710,481, incorporated herein by reference. Sidewall 4 may be formed solely of the calcia refractory.

Although chill 2 and sidewall 4 are shown in Fig. 1 as bodies defining a cylindrical cavity 6, chill 2 and sidewall 4 can be formed to define cavities of any desired configuration to form components, such as, medical prostheses, pump components, gas turbine components such as turbine blades, airframe components, or heat exchangers.

Heating means 10 is a conventional heating means for heating above the liquidus temperature of gamma titanium aluminide alloys, such as an induction heater or tungsten resistance heater. Heating means 10 heats the sidewall 4 above the liquidus temperature of the melt and maintains melt 12 in a molten state. Melt 12 of a gamma titanium aluminide alloy is formed by conventional means such as skull melting and pouring the melt into cavity 6, or melting a solid charge placed in cavity 6 using heating means 10. The skull melting and pouring are performed in the non-oxidizing atmosphere or vacuum surrounding assembly 20. Additional information about skull melting can be found for example in, "Vacuum Arc Skull Melting and Casting," Metals Handbook, 9th Edition, Vol. 15, Casting, ASM International, 1988, pp. 409 to 410, incorporated herein by reference. A conventional directional solidification casting furnace is shown, for example in, "Directional and Monocrystal Solidification," Metals Handbook, 9th Edition, Vol. 15, Casting, ASM International, 1988, pp. 319 to 323, incorporated herein by reference.

Assembly 20 is supported by rod 16 operatively connected to conventional means, not shown, for controlled movement of assembly 20 in the direction of arrow 18. Heating means 10 maintains the temperature of melt 12 above the liquidus temperature of the gamma titanium aluminide alloy. However, a thermal gradient exists between chill surface 2 and melt 12 that causes grains to nucleate and grow on chill surface 2. Mold assemble 20 is maintained in the initial position shown in FIG. 1 for a period of time to allow the grains to nucleate and grow so that the most favorably oriented grains are established. Grains with a preferred growth direction normal to the chill surface grow and crowd out the other grains.

Referring now to FIG. 2, after melt 12 has been held above the liquidus temperature for a period of time to allow grains to nucleate and begin to grow on chill surface 2, the mold assembly 20 is withdrawn from heater 10 in the direction of arrow 18 at a controlled rate. The rate of withdrawal of mold assembly 20 from heater 10 is controlled to allow for directional solidification of solid 14 forming columnar grains 15 extending from the chill surface 2 to melt 12. A thermal gradient having a hot zone above the liquidus temperature of the melt, and a zone below the solidus temperature of the alloy is formed at the interface of solid 14 and liquid 12. The thermal gradient is passed from one end of the melt to the other at a rate that maintains the steady growth of the dendrites 15. A suitable thermal gradient is about 50° to 300° C per inch above the melting temperature of the gamma titanium aluminide alloy, and a suitable travel rate for the thermal gradient is about 1 to 20 inches per hour.

Additional features and advantages of the method of this invention are further shown by the following examples.

Example 1

The first example is performed to show the level of oxygen pickup in a melt of gamma titanium aluminide alloys obtained by conventional skull melting. Several charges of gamma titanium aluminide alloys were formed from high-purity titanium sponge about 99.9% pure, high-purity aluminum about 99.99% pure, and high-purity chromium and niobium about 99.9 percent pure. The charges were placed in a water cooled copper crucible arc melting furnace obtained from Retech, Inc., Ca.. The charges were melted under a protective atmosphere of argon by arc melting using the skull melting method. After the charge was melted the arc was extinguished and the charge was allowed to solidify in the copper crucible. The solidified melt was turned over in the crucible and remelted by the same arc skull melting method to cause further mixing of the melt. The melting was repeated so that the charge was melted a total of three times to form the final casting. The casting was removed from the copper crucible and the oxygen concentration of each casting was analyzed by infrared radiation. The weight, composition, and heating time, of each charge along with the final oxygen content of each casting are shown below in Table 1.

Table 1

Titanium Aluminide Alloys Melted By Skull Melting							
Melt No.	Charge Weight (Grams)	Composition (Atomic Percent)				Heating Time (Minutes)	Oxygen Concentration (Parts Per Million)
		Ti	Al	Cr	Nb		
1.	280	Bal.	48			10 to 15	422
2.	280	Bal.	48			10 to 15	517
3.	280	Bal.	45	2	2	10 to 15	945
4.	280	Bal.	47	2	8	10 to 15	560
5.	280	Bal.	46	2	12	10 to 15	880

Example 2

A calcia crucible comprised of 99 percent purity fused calcia was obtained from Mitsui Zosen Incorporated (USA), New York. Two gamma titanium aluminide alloys were melted by induction heating in the calcia crucibles. Three to four charges were melted in each crucible with a slight variation in the charging procedure for each melt. The charges were formed from high-purity titanium sponge about 99.9% pure, high-purity aluminum about 99.99% pure, and high-purity chromium and niobium about 99.9 percent pure. The charges were formed by placing pieces of the elements in the crucible in the following order:

Melt 1; chromium, niobium, aluminum, titanium,

Melt 2; titanium, aluminum, niobium, chromium,

Melt 3; titanium, aluminum, niobium, chromium,

Melt 4; niobium, chromium, aluminum, titanium,

Melt 5; all four elements melted together, and

Melts 6 and 7; niobium and aluminum melted first followed by chromium and titanium.

Each melt was poured into a graphite or copper mold and the oxygen concentration of each cast melt was analyzed by infrared radiation. The weight, composition, and heating time, of each charge along with the final oxygen content of each casting are shown below in Table 2.

Table 2

Titanium Aluminide Alloys Melted in Calcia Crucible							
Charge No.	Charge Weight (Grams)	Composition (Atomic Percent)				Heating Time (Minutes)	Oxygen Concentration (Parts Per Million)
		Ti	Al	Cr	Nb		
1.	300	Bal.	48	2	8	21	1420
2.	300	Bal.	48	2	8	36	1700
3.	300	Bal.	48	2	4	38	2510
4.	300	Bal.	48	2	4	21	2180
5.	200	Bal.	48	2	4	47	2220
6.	300	Bal.	48	2	4	20	2000
7.	200	Bal.	48	2	8	21	960

In Table 2, charge numbers 1-4 were melted in one crucible, and charge numbers 5-7 were melted in another crucible.

In Table 1 it is shown that conventional skull melting produces a gamma titanium aluminide alloy having an oxygen content from about 422 to 945 parts per million. From Table 2 it can be seen that an appreciable oxygen pickup occurs when a gamma titanium aluminide alloy is melted in the ceramic calcia crucible. However, oxygen pickup is reduced as niobium content is increased. For example, the gamma titanium aluminide alloys having a niobium content of 8 atom percent have greatly reduced oxygen pickup that is about half the oxygen pickup in alloys comprised of 4 atom percent niobium. In addition, the oxygen pickup

for alloys comprised of 8 atom percent niobium is comparable to the oxygen pickup found in skull melting.

Example 3

5 Two gamma titanium aluminide alloy rods comprised of about 46 atom percent aluminum, 10 atom percent niobium, and the balance titanium were prepared by the well known arc melting and drop casting method. A directionally solidified casting of the gamma titanium aluminide was formed in a mold assembly as shown in FIG. 1 comprised of a tungsten-resistance heater and a water-cooled molybdenum chill surface. A calcia sidewall for the mold was obtained from Mitsui Zosen Incorporated (USA), New York. The
10 sidewall had an inner diameter of about 2.5 centimeters and a length of about 12.5 centimeters. The sidewall was sealed on the molybdenum chill surface by an alumina seal. The rods, about 1.9 centimeters in diameter and 5 centimeters in length, were placed in the mold.

The rods were melted by the tungsten-resistance heater encircling the sidewall, and the mold assembly was withdrawn from the tungsten-resistance heater at a rate of about 35 centimeters per hour to provide
15 directional solidification of the melt. A directionally solidified rod of about 2.5 centimeters in diameter and 6.35 centimeters in length having a columnar grain structure with grains about 0.25 centimeter in diameter was formed. Chemical analysis of the directionally solidified rod showed the oxygen concentration to be about 1700 parts per million.

The directionally solidified rod was tested by the well known four point bending method to determine
20 the toughness and in conventional tensile testing to determine the yield strength and plastic fracture strain of the directionally solidified material. The directionally solidified rod had a toughness of about 18 MPa \sqrt{m} , a yield strength of about 675 MPa, and a plastic fracture strain of about 0.75 percent. The directionally solidified rod was heat treated at about 1275° C for 2 hours. The tensile testing was performed at room temperature. The yield strength was again measured at 875° C to be about 580 MPa, and the plastic
25 fracture strain was about 10 percent.

Claims

- 30 1. A method for directional solidification vacuum or protective atmosphere casting a gamma titanium aluminide alloy in a mold comprised of a chill and a sidewall means extending from the chill to form a cavity for holding a molten metal, comprising:
 - forming a melt of the gamma titanium aluminide alloy in the cavity, the melt being comprised of a metal from the group consisting of niobium, tantalum, tungsten, and molybdenum in an effective amount to reduce oxygen pickup in the melt, the sidewall means having at least an inner liner of a
35 calcia refractory facing the melt; and
 - heating the melt in a thermal gradient sufficient to cause directional solidification of the melt from the chill.
- 40 2. A method according to claim 1 wherein the metal is niobium.
3. A method according to Claim 1 or Claim 2 wherein an effective amount is about 2 to 12 atom percent.
4. A method according to any preceding claim wherein an effective amount is about 4 to 8 atom percent.
- 45 5. A method for directional solidification casting a gamma titanium aluminide alloy in a non-oxidizing atmosphere or vacuum and in a mold comprised of a chill and a sidewall means extending from the chill to form a cavity for holding a molten metal, the method comprising:
 - forming the sidewall means to have at least an inner liner of a calcia refractory adjacent the melt;
 - forming a melt of the gamma titanium aluminide alloy in the mold, the melt being comprised of an
50 effective amount of niobium to reduce oxygen pickup in the melt; and
 - heating the melt in a thermal gradient sufficient to cause directional solidification of the melt from the chill.
- 55 6. A method according to claim 5 wherein the metal is niobium.
7. A method according to Claim 5 or Claim 6 wherein an effective amount is about 2 to 12 atom percent.

EP 0 530 968 A1

8. A method according to any one of Claims 5 to 7 wherein an effective amount is about 4 to 8 atom percent.

5

10

15

20

25

30

35

40

45

50

55

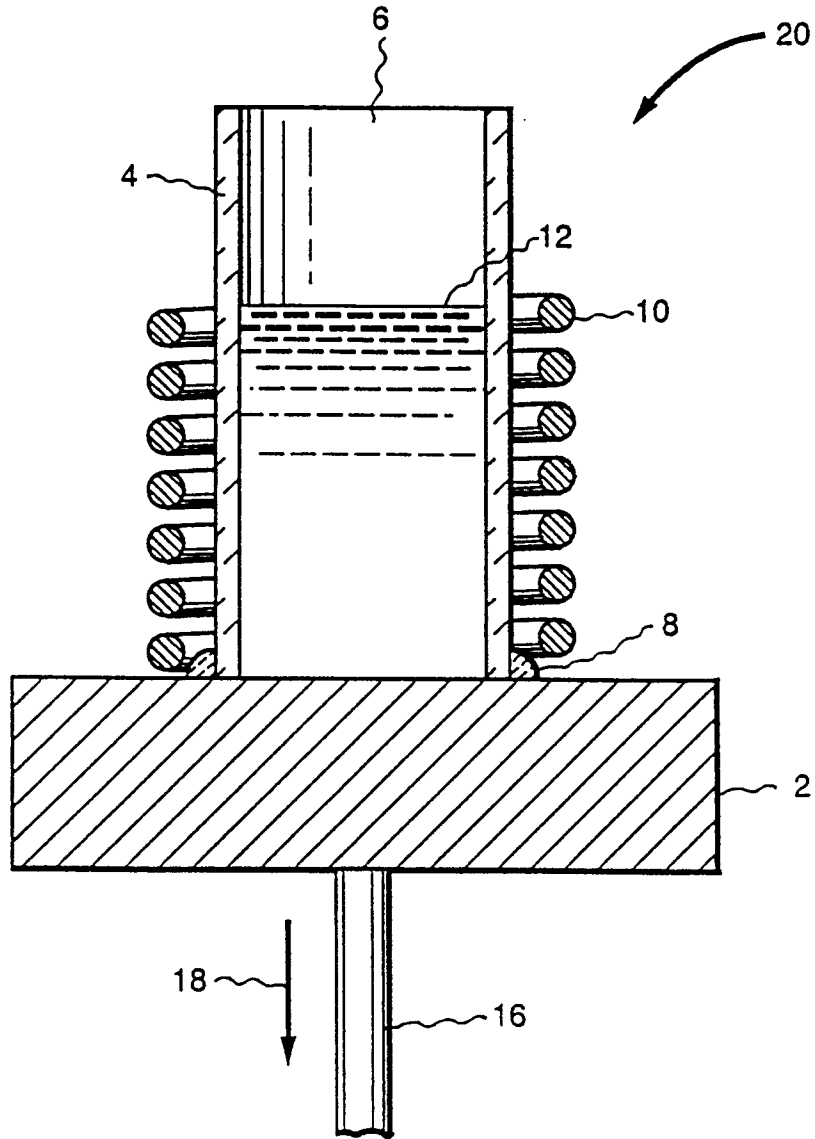


FIG. 1

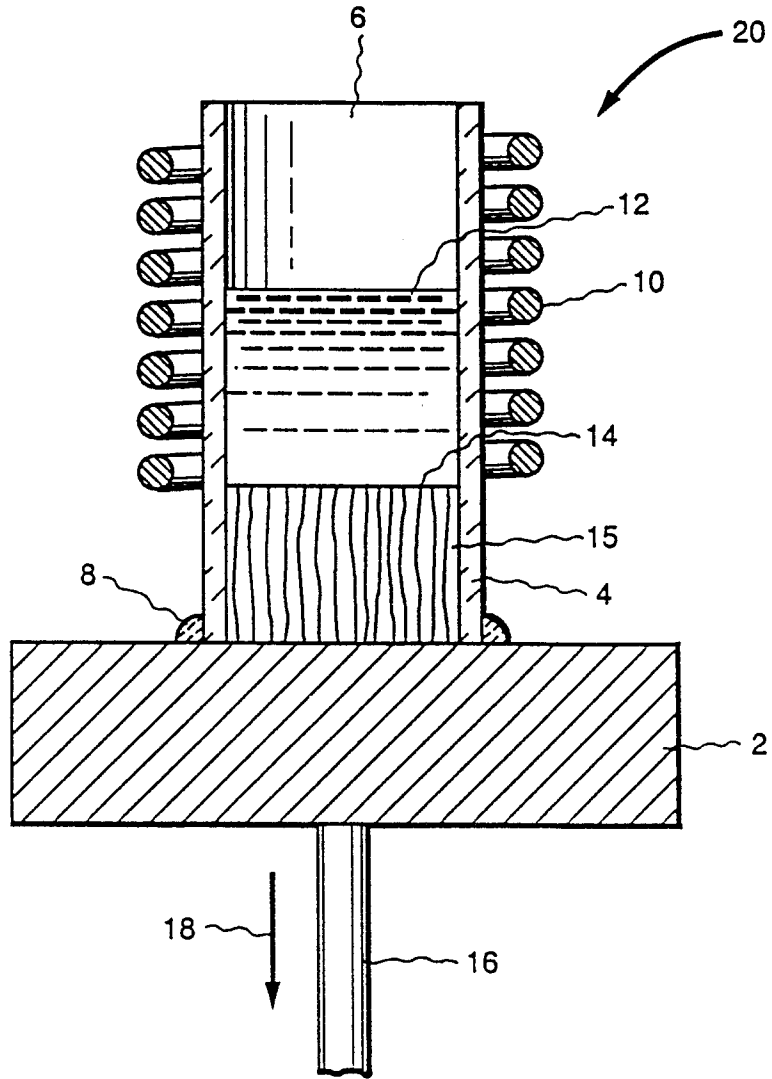


FIG. 2



DOCUMENTS CONSIDERED TO BE RELEVANT			EP 92306862.1
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	<u>EP - A - 0 406 638</u> (GENERAL ELECTRIC) * Table 3 * --	1	C 22 C 1/02 C 22 C 14/00 C 22 C 21/00 B 22 D 27/04
D,A	<u>US - A - 4 294 615</u> (BLACKBURN et al.) * Abstract * --	1	
D,A	<u>US - A - 4 710 481</u> (DEGAWA et al.) * Abstract * --	1	
A	<u>EP - A - 0 092 496</u> (UNITED TECHNOLOGIES) * Abstract; fig. 6 * ----	1,5	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 22 C B 22 D
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
VIENNA		26-11-1992	LUX
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	