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### (54) IMPROVEMENTS IN OR RELATING TO REFRACTORY PRODUCTS

VERBESSERUNGEN AN ODER IN BEZUG AUF FEUERFESTPRODUKTE

AMELIORATIONS CONCERNANT DES PRODUITS REFRACTAIRES

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**EP-A- 0 149 164** **EP-A- 0 282 247**  
**WO-A-88/06500** **WO-A-98/42465**

**EP 1 133 373 B1**

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## Description

[0001] This invention relates to improvements in or relating to refractory products and, more particularly, to improvements in refractory products used in the handling of molten metals to increase reliability under high temperature operating conditions.

[0002] Metal teeming, and in particular the casting of steel usually begins with the metal being melted and transferred to a vessel, e.g. a ladle or tundish. Refractory devices are required, amongst other things, for the regulation of the flow of the molten metal exiting from a nozzle mounted in the bottom of the vessel. In the casting of steel, this is typically applied through an opening in the base of the vessel via nozzles and shrouds into a water-cooled mould. Refractory devices such as sub-entry shrouds and pouring nozzles are often at least partly submerged for long periods of time in the molten metal during the metal teeming process and are therefore subject to high temperatures and stresses during the effective lifetime of the device.

[0003] In a typical teeming process, metal is melted in a furnace, transferred first to a ladle and then to a tundish from which it flows in a controlled manner into a cooled mould. A flow control valve is provided in the tundish comprising a flow control stopper rod selectively engageable with an outlet nozzle seat. The stopper would normally be raised off the seat by a certain amount to achieve a particular rate of flow of molten metal through the valve to ultimately cast a product in a mould.

[0004] The teeming apparatus would usually include a pouring nozzle or a shroud located beneath the flow control valve either of which may be immersed in melt as the casting operation proceeds.

[0005] In an exchange nozzle casting mechanism, the exchange pouring nozzle or shroud is supported beneath a stopper upper nozzle and stationary plate assembly which is used for sealing off the flow of molten metal above the pouring nozzle or shroud to allow the pouring nozzle or shroud to be changed during the teeming process.

[0006] EP-A-0 149 164 discloses a refractory pouring device comprising a ceramic body having a ceramic pouring tube element and a ceramic support tube element. Between said elements there is provided a stock - absorbing interface zone comprising a material being deformable at elevated temperatures.

[0007] EP-A-0 346 378 describes the development of a monotube configuration and compares that to a two part plate and tube assembly generally known and used within an exchange nozzle casting mechanism as described above. The pouring tube element combines a body of high thermal shock resistance and corrosion resistance with a sliding plate surface able to form a tight closure against the stationary components of the mechanism. The sliding plate surface also incorporates a hard edge to permit cutting through any metal skin which may form during the casting operation and which may restrict free movement of the exchange monotube during the replacement procedure.

[0008] An important advantage of the monotube configuration over the original fired plate and tube or cast plate and tube assemblies was the elimination of generally horizontal joints connecting the internal casting bore of the tube with the external atmosphere, thereby eliminating the risk of air ingress or metal leakage across this joint region.

[0009] As casting conditions have become more severe and service life requirements of refractory products increased, new demands have been placed on the monotube elements of an exchange of an exchange nozzle casting mechanism.

[0010] In meeting these demands alternative compositions for the pouring tube element have been developed making it possible to maintain the plate surface and cutting edge configuration whilst providing improved corrosion and erosion resistance. These improved materials for the pouring tube element of a monotube do however exhibit different thermo-mechanical properties from the original materials as shown in the following table:

| MONOTUBE POURING TUBE ELEMENT COMPOSITIONS |                                  |                           |  |
|--------------------------------------------|----------------------------------|---------------------------|--|
| CONVENTIONAL                               |                                  | HIGH CORROSION RESISTANCE |  |
| 40                                         | Al <sub>2</sub> O <sub>3</sub> % | 64                        |  |
| 18                                         | SiO <sub>2</sub> %               | 6                         |  |
| 28                                         | C%                               | 24                        |  |
| 8                                          | ZrO <sub>2</sub> %               | 6                         |  |
| 4                                          | SiC%                             | -                         |  |
| 2.38                                       | Bulk density g/ml                | 2.6                       |  |
| 0.35                                       | Thermal Expansion% 0-1000        | 0.52                      |  |

[0011] In operation, it has been shown that whilst the overall criteria for performance improvement has been met there is an increased risk that thermo mechanical stresses arising at the outset of casting can cause an external micro-crack fracture at the section change between the head and body portions of the pouring tube. In many instances, this micro-crack feature is contained by the inherent integrity of the ceramic body. This results in no operational problem,

but in extreme cases it is possible for the external micro-crack fracture to propagate across the ceramic wall of the tube to the inner bore. This allows either air ingress or metal leakage, both of which cause termination of the cast and possible damage to the exchange nozzle casting mechanism.

**[0012]** Studies of the behaviour of the conventional metallic can and pouring tube element showed that the metallic can, essential to provide the accurate geometry required for a precise fit into the exchange nozzle casting mechanism could also act to transfer heat from the pouring element into the cooled mechanical mechanism, thereby increasing the thermal gradient at this critical point. Additionally at the temperatures experienced during preheat prior to cast start up the lower region of the can would reach a temperature of approx 900°C at which the relatively mild steel from which it is formed loses its rigidity and ceases to provide the desirable structural support below the section change.

**[0013]** A further development of the monotube concept is shown in US 5 866 022 which describes the assembly of a co-pressed, mixed material tube element, as described by EP A 0 346 378 adapted to the desired operational configuration by use of castable materials directly infilling the void between the outer surface of the tube and the inner surface of the metallic support element. This is shown in Figure 4.

**[0014]** Whilst this design concept has shown benefits in terms of reduced incidence of microcrack formation causing in service failures, examination of used pieces shows that a risk remains that a crack will propagate from the angle between the tube and plate sections of the co-pressed tube element, as shown in Fig 5. This behaviour is not of such severe consequence as the failures of the type illustrated in Fig 3 as it does not necessarily result in molten steel leakage. It is however desirable to eliminate this risk.

**[0015]** Extensive computer simulation of the thermo-mechanical stresses arising during preheat and start up of casting has identified the possibility of minimising the stresses leading to such micro crack formation and propagation, by minimising the thermal gradient across the tubular pouring element, providing continuing support below any section change and optimisation of the external geometry of the tubular pouring element.

**[0016]** An object of this invention is to obviate or mitigate the risks of exaggerated thermo mechanical stresses in the new generation of pouring tube elements, and this is found to be achievable by revising both the design of the pouring tube element and the manner in which it is contained within the can. It will be recalled that location of the refractory within the support can requires care to provide the correct geometrical configuration to allow effective operation of the exchange tube mechanism and maintain the principle of no direct horizontal connection from the bore to the exterior other than the machined sliding surface.

**[0017]** According to one aspect of the present invention there is provided a refractory device for use in the teeming of molten metal comprising a ceramic pouring tube element supported in a metallic can, in which a ceramic support element, is encapsulated and a shock - absorbing interface zone between said metallic can and the ceramic pouring tube element, in which zone there is provided a material the thermal properties of which are such that it is substantially solid at ambient temperatures but becomes deformable at the elevated temperatures experienced during metal teeming.

**[0018]** Thus, the interface zone provides continuity of mechanical support to the body portion when in the substantially solid (cool ambient temperature) condition to ensure structural integrity of the assembled refractory device, but deforms sufficiently to provide a buffer against sudden differential thermal stresses, thereby minimising the risks of micro-crack fracture through the body portion due to thermo mechanical stresses during pre-heat and at the start of the casting operation.

**[0019]** Advantageously, the material selected for use in the interface zone is structurally solid at temperatures up to about 700°C and becomes deformable without any appreciable chemical degradation at temperatures above about 700°C. Preferably the material providing the interface zone comprises a pyroplastic ceramic material.

**[0020]** Preferably, the interface zone comprises a ceramic material such as a paste or bonding agent or additional structural ceramic element exhibiting the aforesaid properties.

**[0021]** Conveniently, the pyroplastic material is a frittable composition applied over at least one of the co-operating assembly surfaces of the pouring tube element and the metallic can.

**[0022]** The ceramic support element is normally fully encapsulated within the metallic can, and fits with and around the upper part of the pouring tube element by virtue of said ceramic support element having an internal profile corresponding sufficiently to the external profile of the pouring tube.

Conveniently, the respective profiles are such as to provide corresponding interference fit surfaces or otherwise matching, e.g. tapering surfaces to facilitate assembly, and in-fill or insertion of the required shock-absorbing interface zone material.

**[0023]** The ceramic support element may be pre-formed from a ceramic material of low thermal conductivity, or formed *in situ* by a suitable casting operation of a type familiar to those in this art.

**[0024]** The refractory device may be otherwise finished as is known in the art to suit its intended purpose, e.g. with regard to provision of flat surfaces and outlet nozzles etc.

**[0025]** Embodiments of the invention will now be described with reference to the accompanying drawings in which:

Figure 1 is a cross-sectional view of a two-part plate and tube configuration in accordance with prior art;

Figure 2 is a cross-sectional view of a prior art monotube configuration;

Figure 3 is a cross-sectional view of a monotube configuration showing a stress micro-crack fracture of the type minimised by the present invention;

Figure 4 is a section of modified version of monotube assembly as per US 5 866 022.

Figure 5 is a diagram showing crack mark observed during service trials of such a configuration.

Figure 6 is a cross-sectional view of a refractory device according to one aspect of the present invention; and

Figure 7 is a cross-sectional view of a refractory device according to a second aspect of the present invention.

**[0026]** Referring now to the figures, there is shown in Figures 1-3 cross-sectional views of prior art refractory devices including the two-part plate and tube assembly known generally in the prior art and the early monotube configuration discussed above.

**[0027]** Figure 6 is a cross-sectional view of a refractory product according to one aspect of the present invention. This shows a refractory pouring device having a ceramic pouring tube element **10** such as for example of a pouring nozzle or sub entry shroud. The pouring tube element is supported in a metallic can **11**, which maintains the desired geometrical configuration of the tube for mechanical integrity of the pouring mechanism. A low thermal conductivity ceramic support element **12** is encapsulated within the metallic can, and fits with and around the upper part of the pouring tube element, by virtue of said ceramic support element having an internal profile corresponding sufficiently to the external profile of the pouring tube. Here, a stepped shoulder, interference fit arrangement is illustrated.

**[0028]** The low thermal conductivity of the ceramic support element reduces heat losses from the pouring tube during metal teeming thereby minimising the differential thermal stresses experienced by the pouring tube which could lead to propagation of stress micro-crack features.

**[0029]** A shock absorbing interface zone **13** is formed between the low conductivity ceramic support element **12** and the pouring tube element **10**. The zone is formed in accordance with one aspect of the invention by a layer of pyroplastic ceramic cement, the properties of which are chosen to provide optimum mechanical strength in temperatures below about 700°C to support the pouring tube during preheating operations and manipulation. The cement has a degree of pyroplasticity at elevated temperatures encountered during use of the pouring tube in the metal teeming process to absorb any residual differential stresses, which may be created during this process.

**[0030]** By way of example, the pyroplastic ceramic cement may be formed from an alumina-silicate mixture with an addition of fluxing agents to generate the pyroplastic behaviour. A typical analysis of said pyroplastic cement being alumina 20%, silica 54%, potassium oxide 6%, boric oxide 12% and sodium oxide 8%.

**[0031]** Such a composition will provide for progressive melting from about 700°C to impart plasticity to the layer.

**[0032]** Figure 7 illustrates a further embodiment of the present invention wherein the pouring tube element **20** is coated with a pyroplastic surface layer **24** on its upper region to provide the desired low temperature rigidity and high temperature malleability. The coated tube is then encapsulated within the metallic can **21** by a ceramic concrete **22**, which provides mechanical support to the pouring tube during the teeming process. Furthermore, the ceramic support element reduces heat losses from the pouring tube during metal teeming thereby minimising the differential thermal stresses experienced by the pouring tube which lead to propagation of stress microcrack features.

**[0033]** In use of either of the refractory device described above, the pouring tube is mounted beneath the orifice of a vessel (not shown). Molten metal is poured through the pouring tube for example into a water-cooled mould (not shown). During the metal casting process, the external temperature of the pouring tube rises typically to between 700°C and 900°C. At temperatures up to about 700°C, the pyroplastic interface zone (**13**; **24**) between the pouring tube element (**10**; **20**) and the ceramic element (**12**; **22**) encapsulated in the metallic can remains solid and provides structural continuity and additional mechanical support to the pouring tube. Thereby, structural integrity of the refractory device is provided for e.g. during handling for transport purposes, and initially during assembly into a pouring mechanism and pre-heat. At temperatures above about 700°C however, at which differential thermal stresses between the pouring tube and the support therefor in the metallic can would have previously possibly caused a stress micro-crack fracture of the pouring tube, the pyroplastic interface zone becomes deformable, thereby minimising differential thermal stresses experienced by the pouring tube in the region supported by the metallic can. Therefore, in this way the possibility of micro-crack fracture through the refractory device and failure thereof is obviated or mitigated. Thus, the present invention results in an improved refractory device that has better reliability and is less prone to damage from differential stress micro-crack features.

## Claims

1. A refractory device for use in the teeming of molten metal, comprising a ceramic pouring tube element 10, supported in a metallic can 11, in which a ceramic support element 12 is encapsulated and a shock-absorbing interface zone 13 between said metallic can 11 and the ceramic pouring tube element 10, in which zone there is provided a material the thermal properties of which are such that it is substantially solid at ambient temperatures but becomes deformable at elevated temperatures experienced during metal teeming.
2. A refractory device according to claim 1, wherein the material selected for use in the interface zone 13 is structurally solid at temperatures up to about 700°C and becomes deformable without any appreciable chemical degradation at temperatures above about 700 °C.
3. A refractory device according to claim 1 or 2, wherein the material providing the interface zone 13 comprises a pyroplastic ceramic material.
4. A refractory device according to claim 1, wherein the interface zone 13 comprises a ceramic material such as a paste or bonding agent or additional structural ceramic element.
5. A refractory device according to claim 3, wherein the pyroplastic material is a frittable composition applied over at least one of the co-operating assembly surfaces of the pouring tube element and the metallic can.
6. A refractory device according to any one of the preceding claims, wherein the ceramic support element 12 is fully encapsulated within the metallic can 11, and fits with and around the upper part of the pouring tube element 10 by virtue of said ceramic support element (12) having an internal profile corresponding sufficiently to the external profile of the pouring tube.
7. A refractory device according to claim 6, wherein the respective profiles are such as to provide corresponding interference fit surfaces or otherwise matching.
8. A refractory device according to any one of the preceding claims, wherein the ceramic support element 12 is pre-formed from a ceramic material of low thermal conductivity, or formed *in situ* by a suitable casting operation.
9. A refractory device according to any one of the preceding claims, wherein the refractory device is finished to suit its intended purpose.

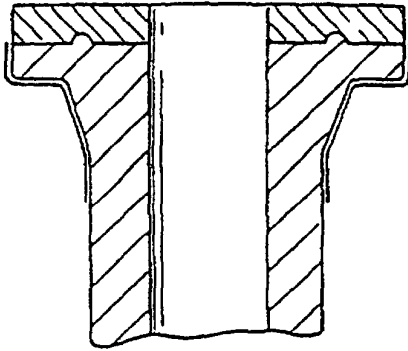
## Patentansprüche

1. Feuerfeste Einrichtung zum Gießen einer Metallschmelze, mit einem rohrförmigen keramischen Gießelement 10, welches in einer metallischen Aufnahme 11 gehalten wird, in der ein keramisches Trägerelement 12 eingeschlossen ist, und einer schockabsorbierenden Zwischenzone 13 zwischen der metallischen Aufnahme 11 und dem rohrförmigen keramischen Gießelement 10, wobei in dieser Zone ein Material vorgesehen ist, dessen thermische Eigenschaften so sind, dass es bei Umgebungstemperatur im Wesentlichen fest ist aber bei erhöhten Temperaturen wie sie beim Metallguß auftreten, deformierbar wird.
2. Feuerfeste Einrichtung nach Anspruch 1, bei der das Material, welches zur Verwendung in der Zwischenzone 13 ausgewählt wurde, bei Temperaturen bis etwa 700 °C strukturell fest ist und ohne wesentliche chemische Zersetzung bei Temperaturen oberhalb etwa 700 °C deformierbar wird.
3. Feuerfeste Einrichtung nach Anspruch 1 oder 2, bei der das Material, welches die Zwischenzone 13 bildet, ein pyroplastisches keramisches Material umfaßt.
4. Keramische Einrichtung nach Anspruch 1, bei der die Zwischenzone 13 ein keramisches Material wie eine Paste oder ein Bindemittel oder ein zusätzliches strukturelles keramisches Element umfaßt.
5. Feuerfeste Einrichtung nach Anspruch 3, bei der das pyroplastische Material eine sinterbare Zusammensetzung ist, die über wenigstens eine der korrespondierenden Oberflächen von rohrförmigem Gießelement und metallischer Aufnahme aufgebracht ist.

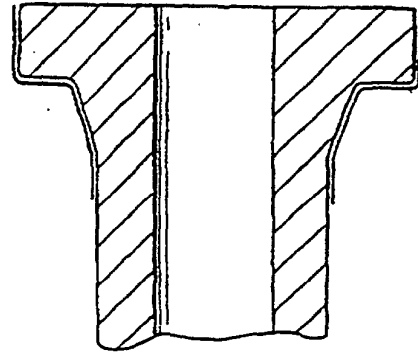
6. Feuerfeste Einrichtung nach einem der vorhergehenden Ansprüche, bei der das keramische Trägerelement 12 vollständig innerhalb der metallischen Aufnahme 11 eingeschlossen ist und mit und um den oberen Teil des rohrförmigen Gießelementes durch das genannte keramische Trägerelement 12 angepaßt ist, welches ein inneres Profil aufweist, welches im Wesentlichen dem äußeren Profil des Gießrohres entspricht.
7. Feuerfeste Einrichtung nach Anspruch 6, bei der die wechselseitigen Profile so sind, um korrespondierende Zwischenoberflächen oder andere Paßformen bereitzustellen.
8. Feuerfeste Einrichtung nach einem der vorhergehenden Ansprüche, wobei das keramische Trägerelement 12 aus einem keramischen Material geringer thermischer Leitfähigkeit vorgeformt ist oder in situ durch Gießen geformt ist.
9. Feuerfeste Einrichtung nach einem der vorhergehenden Ansprüche, wobei die feuerfeste Einrichtung so bearbeitet ist, dass sie dem beanspruchten Zweck genügt.

## Revendications

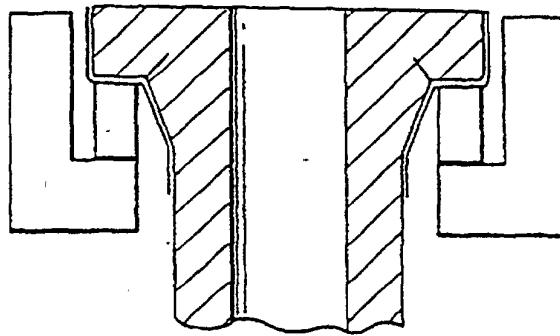
1. Dispositif réfractaire pour la coulée du métal fondu, comprenant un élément de tube verseur en céramique 10, maintenu dans un bidon métallique 11, dans lequel un élément de support en céramique 12 est encapsulé, et une zone d'interface amortissante 13 entre ledit bidon métallique 11 et l'élément de tube verseur en céramique 10, laquelle zone est dotée d'un matériau dont les propriétés thermiques sont telles, qu'il reste solide aux températures ambiantes, mais subit des déformations à des températures élevées, éprouvées pendant la coulée du métal.
2. Dispositif réfractaire selon la revendication 1, dans lequel le matériau sélectionné pour être utilisé dans la zone d'interface 13, est structurellement solide à des températures allant jusqu'à 700°C environ, mais subit des déformations sans dégradation chimique notable, à des températures supérieures à 700°C environ.
3. Dispositif réfractaire selon la revendication 1 ou 2, dans lequel le matériau constituant la zone d'interface 13 comprend un matériau pyroplastique en céramique.
4. Dispositif réfractaire selon la revendication 1, dans lequel la zone d'interface 13 comprend un matériau en céramique tel qu'une pâte, un liant ou un élément en céramique structurel supplémentaire.
5. Dispositif réfractaire selon la revendication 3, dans lequel le matériau pyroplastique est une composition susceptible d'être frittée appliquée sur au moins une des surfaces d'assemblage coopérantes de l'élément de tube verseur et du bidon métallique.
6. Dispositif réfractaire selon une quelconque des revendications précédentes, dans lequel l'élément de support 12 est complètement encapsulé dans le bidon métallique 11, et est assemblé avec et autour de la partie supérieure de l'élément de tube verseur 10, et ce du fait que ledit élément de support en céramique 12 a un profil interne correspondant suffisamment au profil externe du tube verseur.
7. Dispositif réfractaire selon la revendication 6, dans lequel les profils respectifs sont conçus de telle sorte qu'ils présentent des surfaces correspondantes ajustées de façon serrée ou s'épousant d'une autre manière.
8. Dispositif réfractaire selon une quelconque des revendications précédentes, dans lequel l'élément de support en céramique est préformé à partir d'un matériau en céramique de faible conductibilité thermique, ou formé in situ par une opération de moulage appropriée.
9. Dispositif réfractaire selon une quelconque des revendications précédentes, dans lequel le dispositif réfractaire est réalisé pour répondre à l'objectif fixé.



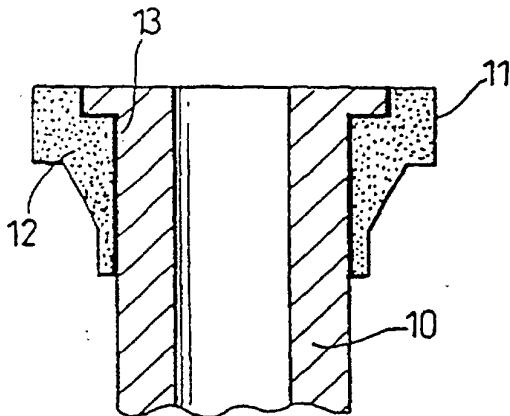
*Fig. 1 (PRIOR ART)*



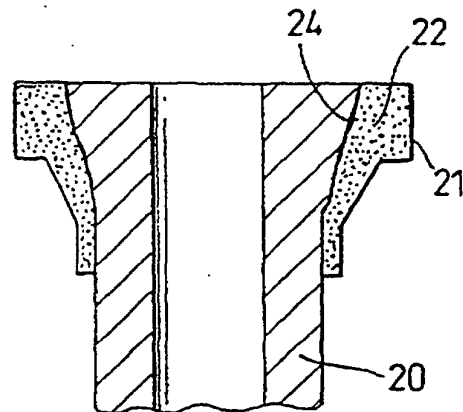
*Fig. 2 (PRIOR ART)*



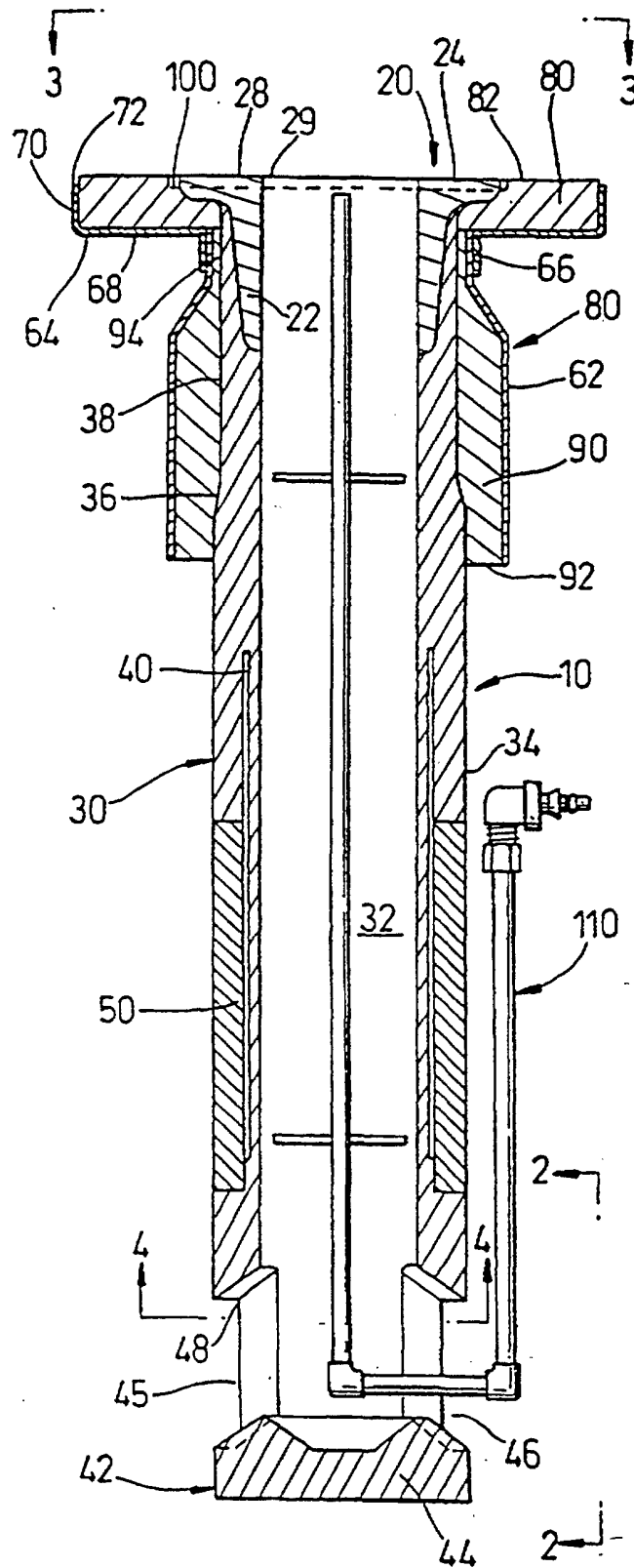
*Fig. 3 (PRIOR ART)*



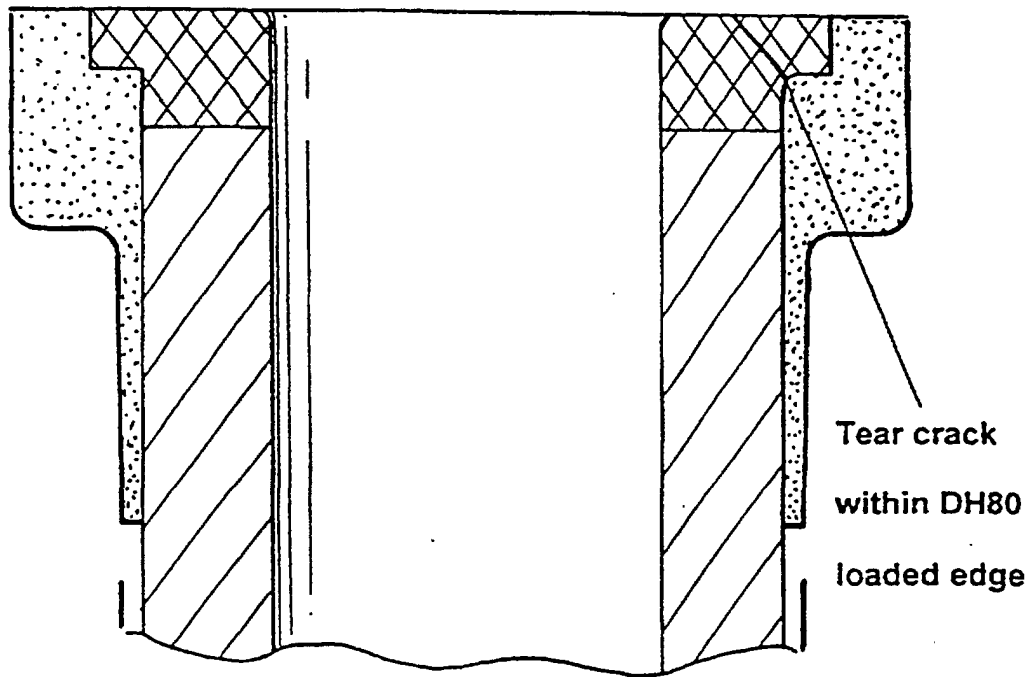
*Fig. 6*



*Fig. 7*



*Fig. 4*



*Fig. 5*