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(54) CHILL CASTING OF METAL STRIP EMPLOYING A MOLYBDENUM CHILL SURFACE.

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Chill casting of metal strip employing a molybdenum chill surface

This invention relates to a method and apparatus for making amorphous metal strip by impinging molten metal onto the surface of a rapidly moving chill body.

It is known to make flat, continuous metal strip, of crystalline as well as amorphous (glassy) structure, directly from the melt by impinging molten metal onto the flat surface of a rapidly moving chill body whereon it is quenched to the solid state. The chill body may be flat, at least in a direction transverse to the direction of movement of the chill body, so that it can be a rotating wheel or travelling belt, usually an endless belt, and the molten metal is impinged onto the flat peripheral surface of the wheel or belt (see DE—A—2746238). The surface of the chill body is disclosed in this reference as being of a metal of relatively high thermal conductivity such as copper, and the metal is impinged onto the surface of the chill body through a slotted nozzle located in close proximity to the chill surface, with the slot generally perpendicular to the direction of movement of the chill surface.

It is also known to form metal filament directly from the melt by contacting a pendant, unconfined drop of molten metal with the V-shaped circumferential edge or lip of a rotating heat extraction member, as disclosed, for example in Patents US—A—3,896,203 and US—A—4,124,664. The pendant drop methods disclosed in these patents may employ a heat extracting edge or lip composed of metals such as copper, aluminum, nickel, molybdenum and iron. These methods, however, do not produce flat strip, but instead produce what appears to be rounded fibers, having opposed convex/concave surfaces.

The surface of the chill body must meet several requirements. First, in the quench casting method it must be wetted by the molten metal or else formation of continuous strip will not take place, but in the pendant drop method it should not be wet by the molten metal to the extent that the drop is destabilised. Second, it must be non-reactive with the molten metal, that is to say the molten metal must not attack, and must not weld to the chill surface, or else the strip cannot be cleanly separated therefrom. Third, it must have good thermal conductivity to permit rapid removal of large amounts of heat as is necessary to effect rapid solidification of the molten metal. Lastly, for the quench casting method, it must have sufficient wear resistance to resist continuous impingement by molten metal in the continuous production of metal strip. Wear resistance is an extremely important aspect of chill body performance in the quench casting method since severe erosion of the chill surface usually results from a combination of factors, including the momentum of the impinging stream of molten metal in combination with the high temperature of the molten metal, but does not usually pose a problem in the pendant drop method.

High heat conductivity metals previously proposed to serve as chill body surface, such as copper, aluminum, beryllium, copper or silver, do not have the wear characteristics required for satisfactory performance in the quench casting method. Others, such as stainless steel, which would be expected to have good wear characteristics, fall short in other respects, such as failure to provide sufficient wetting.

In accordance with the present invention there is provided an improvement in the method for making amorphous metal strip directly from the melt by impinging the molten metal, which upon rapid cooling from the melt forms an amorphous solid body, onto the surface of a rapidly moving chill body, said surface being flat at least in a direction transverse to the direction of movement of the chill body, to quench the metal into a flat, predominantly amorphous continuous metal strip, which improvement comprises impinging the molten metal onto the flat surface of a chill body made of molybdenum.

The present invention further provides an improvement in the apparatus for making metal strip directly from the melt by impinging molten metal onto the flat surface of a rapidly moving chill body, which apparatus includes a chill body having a surface which is flat at least in the direction transverse to the direction of movement of the chill body, said surface being adapted to receive molten metal to be impinged thereon for rapid quenching to the solid state, and means functionally connected with said chill body for impinging molten metal onto its surface, wherein the improvement comprises providing a chill body having a surface of molybdenum.

It has surprisingly been found that the molybdenum chill surface is readily wetted by molten metal, especially by iron, nickel or cobalt-based alloys, which upon rapid quenching from the melt form amorphous structures. The molybdenum surface further provides for good adhesion of the solidified metal strip, which is essential to effect thorough quenching of the metal if a ductile, amorphous metal strip is desired, yet it also affords clean release of the solidified strip from the surface. Most importantly, the molybdenum surface has excellent wear-resistant properties as compared to chill surfaces previously used in the quench casting method. In addition, the molybdenum has adequate heat conductivity to permit sufficiently rapid quenching, at rates in excess of 10^4 or 10^5 degrees centigrade per second, of thin layers of molten metal (in the order of a few mils (1 mil = 25.4 micrometer) thickness), as is required for formation of amorphous metal strip.

The benefits of chill bodies having a molybdenum surface in the process of making flat metal strip directly from the melt by impinging the molten metal onto the rapidly moving flat surface of a chill body are obtained regardless of the configuration of the chill body. That is to say, the chill body may be a rapidly rotating drum having a flat exterior surface which serves as the chill surface; it may be a rapidly rotating cylinder whereof the flat inner surface furnishes the chill surface, a moving belt or any other suitable structure which provides a flat surface.

For purposes of the present invention, a flat strip is a slender body whose transverse dimensions are much less than its length, and whose thickness is much less than its width, typically having a width at least about ten times its thickness, and having smooth and even top and bottom surfaces which are generally parallel to each other.

A flat chill body surface is an endless surface provided by an endless belt, or the exterior or interior surface of a drum or cylinder, and which is smooth and even and which is straight in transverse direction, upon which a flat strip, as above-defined, may be cast.

The annexed drawings further illustrate the present invention.

Fig. 1 is a cross-sectional view of an annular chill roll, the exterior surface of which is provided with a layer of molybdenum metal, to provide a casting surface of molybdenum.

Fig. 2 is a cross-sectional view of an annular chill roll having a ring of molybdenum inserted in its surface.

Fig. 3 is a cross-sectional view of a cylindrical chill body having an inner molybdenum-clad chill surface inclined with respect to the axis of rotation.

Fig. 4 is a side view in partial cross section showing means for jetting molten metal onto a rotating chill roll and a rotating chill roll provided with a chill surface of molybdenum metal.

Fig. 5 is a somewhat simplified perspective view of apparatus including means for depositing molten metal onto a chill surface in the form of a moving endless belt having a surface of molybdenum.

Chill casting processes for making flat metal strip — polycrystalline as well as amorphous (glassy) metal strip — by impinging molten metal onto the flat surface of a rapidly moving chill surface of a heat extracting member (chill body) are well known. It has now been found that for use in such chill casting processes molybdenum has a desirable combination of properties required of a good chill surface, namely high melting point (2650°C); relatively low coefficient of thermal expansion (lower than that of copper); moderately high thermal conductivity (about 35% of that of copper); and moderately high hardness. It has further been found that molybdenum has the required wetting properties for the molten metal and release properties for the solidified strip which, in combination with the aforementioned properties, make it eminently suitable for use as chill surface in quench casting of amorphous metal strips, especially ductile amorphous metal strips. Most significant is the ability of molybdenum chill surfaces to resist erosion and wear by the impinging stream of molten metal, whether the casting takes place under vacuum or in a gaseous atmosphere, which may be air or a protective atmosphere such as nitrogen, helium and the like. This is in contrast to the presently employed copper chill surfaces.

When flat amorphous metal strips are made by jetting molten glass forming alloy against the surface of a rapidly rotating chill body as, e.g., described in US—A—4,077,462 to Bedell et al., or in US—A—3,856,074 to Kavesh, the surface of the chill body becomes gradually eroded. A rough, uneven track is developed around the periphery of the chill body surface whereon casting of the strip takes place. Further casting into the same track produces strip of unacceptable quality, having a rough surface and ragged edges. The problem of chill surface wear in these processes is even more acute when casting takes place under vacuum. The absence of an intervening gas layer in vacuum casting allows a larger area of the chill surface to be impacted and wetted by the molten jet. Another factor which leads to severe wear on conventional chill surfaces is inclusion in the alloy being cast of appreciable amounts of refractory metals, e.g., molybdenum, tungsten, chromium, hafnium, iridium, niobium, osmium, platinum, rhenium, rhodium, ruthenium, tantalum, thorium, vanadium, and zirconium. Hence, use of a chill surface of molybdenum is particularly advantageous when casting under vacuum (say under absolute pressure of less than 1 in. Hg. (3.39 KPa)), or when casting glass-forming alloys containing one or more refractory metals, and especially when casting such alloys under vacuum.

The form of the chill body and the mode of the casting operation are not critical for purposes of the present invention, so long as a flat casting surface is provided. For example, casting may take place against the peripheral surface of a rapidly rotating drum by jetting molten metal against that surface, as disclosed in the above-mentioned patents to Bedell et al. and Kavesh. The molten metal may be deposited under pressure from a slotted nozzle onto the flat chill surface, as described in US—A—4,142,571 to Narasimhan. Furthermore, the chill surface may be furnished by the interior surface of a rotating cylinder, as described in US—A—3,881,540 to Kavesh and US—A—3,881,542 to Polk et al., or as shown by Pond and Maddin in *Trans. Met. Soc.* AIME, 245 (1969) 2,475—6.

The chill surface of molybdenum may, in accordance with the present invention, be provided by fabricating the chill body of molybdenum, or by merely providing a surface layer of molybdenum on a chill body constructed of other material, suitably material having high thermal conductivity such as copper or silver. Chill bodies made of molybdenum may be fabricated employing methods usually employed for fabrication of molybdenum, including machining from solid stock, such as cast pieces, or fabrication by known powder metallurgical methods. A particularly desirable embodiment of the present invention is a composite chill body, especially a chill roll, made of copper provided with a hoop of molybdenum, as illustrated in Figs. 1 and 2. With reference to Fig. 1, chill roll 1 made of copper is mounted for rotation on shaft 2. The flat exterior surface of chill roll 1 is provided with a hoop of molybdenum 3. In Fig. 1, the hoop of molybdenum covers the total peripheral surface of the chill roll. With reference to Fig. 2, a narrower hoop of molybdenum 3 is provided covering only part of the peripheral surface of the chill roll. The molybdenum hoop may be affixed to the copper chill roll, e.g. by shrink fitting. Alternatively, a molybdenum surface may be provided by any other conventional surface coating method, as for example oxyacetylene spraying, a method which involves feeding a molybdenum wire into the cone of an oxygen/acetylene flame to melt the metal, and then propelling the molten metal in droplet form against the surface to be coated. Other suitable methods include plasma arc spraying and conventional cladding procedures.

Detailed design and construction of apparatus of the present invention is within the capability of any competent worker skilled in the art.

The following example further illustrates the present invention and sets forth the best mode presently contemplated for its practice.

Example 1

Apparatus employed was similar to that depicted in Fig. 4 employing a chill roll of construction as shown in Fig. 2. The chill roll had an outer diameter of 8 inches (20 cm), and its quench surface was 0.5 inches (1.3 cm) wide. It was rotated at a speed of about 2000 rpm. The apparatus was enclosed in a vacuum chamber. All tests were conducted under vacuum of about 100 mm Hg (13 MPa). Concurrent experiments employing a chill roll made of copper having an outer diameter of 8 inches (20 cm) and a width of 1 inch (2.5 cm) rotated at 2000 rpm, were conducted, also under vacuum of about 100 mm Hg (13 MPa). A number of different glass forming alloys (alloys which upon rapid quenching from the melt, at a rate in excess of about 10^4 to 10^5 °C/sec. form an amorphous solid structure (see, e.g. U.S.P. 3,856,513 to Chen and Polk) having melting points in excess of 1,500°C were cast by jetting the molten metal against the rotating chill surface through an orifice of 0.025 inch (0.6 mm) diameter under pressure of 5 psig (34 KPa). It was difficult to cast continuous ductile strips on the copper chill surface. In all cases the molten alloys attacked the copper chill surface, causing erosion, cracking and pitting. The chill surface so roughened caused subsequent mechanical locking of pieces of strip onto the chill surface along the track where the strip was cast. The pieces of strip welded to or mechanically interlocked with the chill surface, causing disintegration of the molten puddle on the chill surface, and prevented subsequent formation of continuous strip on the same track. The yield of usable strip was very low. In contrast thereto the same alloys, when cast on a molybdenum chill surface, yielded good quality ribbon. The comparative results are summarized in Table 1, below.

TABLE I
Results of Chill Casting of 30 gms of Molybdenum and Tungsten Base Glassy Alloys on Copper and Molybdenum Chill Surfaces

Copper Chill Surface

Alloy Composition (atom percent)	Ribbon Fabricability	Ribbon Characteristics	Chill Surface Condition after Casting	Yield of Ribbon
$Mo_{40}Co_{40}B_{20}$	Extremely poor	Discontinuous — rough edge	Gorged; metal pieces welded to surface	2%
$Mo_{40}Fe_{40}B_{20}$	ditto	ditto	ditto	2%
$Mo_{50}Co_{30}B_{20}$	ditto	ditto	ditto	2%
$Mo_{50}Fe_{30}B_{20}$	ditto	ditto	ditto	2%
$Mo_{60}Fe_{20}B_{20}$	ditto	ditto	ditto	2%
$Mo_{65}Fe_{15}B_{20}$	ditto	ditto	ditto	2%
$W_{40}Fe_{20}Co_{20}B_{20}$	ditto	ditto	ditto	2%
$W_{40}Ni_{50}B_{10}$	ditto	ditto	ditto	2%
$Mo_{45}Ni_{45}B_{10}$	ditto	ditto	ditto	2%
$W_{40}Co_{50}B_{10}$	ditto	ditto	ditto	2%
$Mo_{60}Co_{20}B_{20}$	ditto	ditto	ditto	2%
$Mo_{30}W_{20}Fe_{30}B_{20}$	ditto	ditto	ditto	2%
$Mo_{45}Fe_{10}Ni_{10}Co_{15}B_{20}$	ditto	ditto	ditto	2%
$Mo_{50}Fe_{20}Co_{10}B_{20}$	ditto	ditto	ditto	2%
$Mo_{40}Fe_{20}Co_{20}B_{20}$	ditto	ditto	ditto	2%
$Fe_{47}W_{35}B_{18}$	ditto	ditto	ditto	2%
$Mo_{40}Fe_{33}Cr_{7}B_{20}$	ditto	ditto	ditto	2%
$W_{40}Fe_{50}B_{10}$	ditto	ditto	ditto	2%
$Fe_{40}W_{40}B_{20}$	ditto	ditto	ditto	2%
$Ni_{50}Mo_{30}B_{20}$	ditto	ditto	ditto	2%
Molybdenum Chill Surface				
$Mo_{40}Co_{40}B_{20}$	Excellent	Continuous — good edge and surface	Insignificant wear	90%
$Mo_{40}Fe_{40}B_{20}$	ditto	ditto	ditto	90%
$Mo_{50}Co_{30}B_{20}$	ditto	ditto	ditto	90%
$Mo_{50}Fe_{30}B_{20}$	ditto	ditto	ditto	90%
$Mo_{60}Fe_{20}B_{20}$	ditto	ditto	ditto	90%

TABLE I (Continued)

Alloy Composition (atom percent)	Ribbon Fabricability	Ribbon Characteristics	Chill Surface Condition after Casting	Yield of Ribbon
$Mo_{65}Fe_{15}B_{20}$	ditto	ditto	ditto	90%
$W_{40}Fe_{20}Co_{20}B_{20}$	ditto	ditto	ditto	90%
$W_{40}Ni_{50}B_{10}$	ditto	ditto	ditto	95%
$Mo_{45}Ni_{45}B_{10}$	ditto	ditto	ditto	95%
$W_{40}Co_{50}B_{10}$	ditto	ditto	ditto	95%
$Mo_{60}Co_{20}B_{20}$	ditto	ditto	ditto	90%
$Mo_{30}W_{20}Fe_{30}B_{20}$	ditto	ditto	ditto	90%
$Mo_{45}Fe_{10}Ni_{10}Co_{15}B_{20}$	ditto	ditto	ditto	90%
$Mo_{50}Fe_{20}Co_{10}B_{20}$	ditto	ditto	ditto	90%
$Mo_{40}Fe_{20}Co_{20}B_{20}$	ditto	ditto	ditto	90%
$Fe_{47}W_{35}B_{18}$	ditto	ditto	ditto	90%
$Mo_{40}Fe_{33}Cr_{7}B_{20}$	ditto	ditto	ditto	90%
$W_{40}Fe_{50}B_{10}$	ditto	ditto	ditto	90%
$Fe_{40}W_{40}B_{20}$	ditto	ditto	ditto	90%
$Ni_{50}Mo_{30}B_{20}$	ditto	ditto	ditto	90%

Example 2

Following the general procedure of Example 1, 50 gram portions of molten, glass-forming alloy of the composition $Fe_5Ni_{45}B_{18}Mo_4Cr_{10}Co_{20}$ (atom percent) were impinged (squirted) on to the flat peripheral surface of chill rolls of 8—12 in. (20 to 30 cm) diameter fabricated of different materials of construction and the quality of the strip (whether or not ductile, glassy metal strip was obtained), and chill surface wear and casting qualities were visually observed. Results are summarized in Table 2, below.

TABLE 2

Chill Surface Material	Makes Ductile Strip	Remarks:
Nickel	No	Melt welds to substrate at spots, jet breaks up on impingement.
Monel™ ($Ni_{60}Cu_{40}$)	Yes	Only limited lengths; melt welds to substrate as beads.
Cupronickel	No	Melt does not wet, puddle breaks up.
Stainless 304 Cold Rolled Mild Steel	No	Same as above.
Tool Steel (hardened)	No	Melt welds to the substrate at spots.
Chromeplate (.001″ = 0.025 mm) on Hardened Tool Steel	Yes	Makes continuous ribbons, no spalling of chromium.
Invar™ (Fe—Ni)	No	Melt welds to the substrate.
Chromeplate (.001″ = 0.025 mm) on Invar™	Yes	Makes good ribbon, no spalling of chromium.
Chromeplate (.001″ = 0.025 mm) on Copper	Yes	Only limited lengths, chromium spalls off afterwards.
Molybdenum (hot pressed, 95% dense)	Yes	Makes continuous ribbons.
BeO (hot pressed, 90% dense)	No	Puddle breaks up.
Pyrex™	No	Puddle breaks up.
Tungsten (chemical vapor deposited, 100% dense)	Yes	Makes ribbon.
Platinum	No	Puddle breaks up, melt does not wet the substrate.

Claims

1. A method for making an amorphous metal strip directly from the melt by impinging molten metal, which upon rapid cooling from the melt forms an amorphous solid body, onto the surface of a rapidly moving chill body, said surface being flat at least in a direction transverse to the direction of movement of the chill body, to quench the metal into a flat, predominantly amorphous continuous metal strip, characterised in that the flat surface of the chill body is made of molybdenum.

2. A method according to claim 1 conducted under vacuum of absolute pressure of less than 1 inch Hg (3.4 kPa).

3. A method according to claim 1 or 2 wherein the molten metal is an alloy containing one or more refractory metals.

4. Apparatus for making metal strip directly from molten metal by impinging the molten metal onto the flat surface of rapidly moving chill body, comprising a chill body having a surface which is flat at least in the direction transverse to the direction of movement of the chill body, said surface being adapted to receive molten metal to be impinged thereon for rapid quenching to the solid state, and means functionally cooperating with said chill body for impinging molten metal onto its surface, characterised in that the flat surface of the chill body is made of molybdenum.

5. Apparatus according to claim 4 when enclosed in a vacuum chamber.

6. Apparatus according to claim 4 or 5 wherein the chill body is of copper provided with a chill surface of molybdenum.

7. Apparatus according to claim 4, 5 or 6 wherein the chill body is an annular chill roll having a peripheral chill surface of molybdenum.

8. Apparatus according to claim 4, 5 or 6 wherein the chill body is a cylindrical chill body having an internal chill surface of molybdenum.

Revendications

1. Procédé de fabrication d'une bande en métal amorphe directement à partir de l'état fondu par projection de métal à l'état fondu, qui lors d'un refroidissement rapide à partir de l'état fondu forme un corps solide amorphe, sur la surface d'un corps de refroidissement se déplaçant rapidement, la surface étant plate tout au moins dans une direction transversale au sens de déplacement du corps de refroidissement, dans le but de tremper le métal pour le transformer en bande métallique continue, plate, principalement amorphe, caractérisé en ce que la surface plate du corps de refroidissement est en molybdène.

2. Procédé selon la revendication 1, caractérisé en ce qu'il est conduit sous un vide ayant une pression absolue inférieure à 3,4 kPa.

3. Procédé selon la revendication 1 ou 2, caractérisé en ce que le métal à l'état fondu est un alliage contenant un ou plusieurs métaux réfractaires.

4. Dispositif de fabrication d'une bande métallique directement à partir d'un métal à l'état fondu par projection du métal à l'état fondu sur la surface plate d'un corps de refroidissement se déplaçant rapidement, comprenant un corps de refroidissement ayant une surface qui est plate tout au moins dans la direction transversale au sens de déplacement du corps, cette surface étant destinée à être frappée par le métal à l'état fondu pour provoquer une trempe rapide jusqu'à l'état solide, et un moyen coopérant de manière active avec le corps de refroidissement pour projeter le métal à l'état fondu sur sa surface, caractérisé en ce que la surface plate du corps de refroidissement est en molybdène.

5. Dispositif selon la revendication 4, caractérisé en ce qu'il est enfermé dans une chambre sous vide.

6. Dispositif selon la revendication 4 ou 5, caractérisé en ce que le corps de refroidissement est en cuivre revêtu d'une surface de refroidissement en molybdène.

7. Dispositif selon la revendication 4, 5 ou 6, caractérisé en ce que le corps de refroidissement est un rouleau de refroidissement annulaire ayant une surface périphérique de refroidissement en molybdène.

8. Dispositif selon la revendication 4, 5 ou 6, caractérisé en ce que le corps de refroidissement est un corps de refroidissement cylindrique comportant une surface de refroidissement intérieure en molybdène.

Patentansprüche

1. Verfahren zur Herstellung eines amorphen Metallstreifens direkt aus der Schmelze durch Auftreffenlassen von geschmolzenem Metall, das bei raschen Abkühlen aus der Schmelze einen amorphen festen Körper bildet, auf die Oberfläche eines sich schnell bewegenden Abkühlkörpers, dessen Oberfläche wenigstens in einer Richtung quer zur Bewegungsrichtung des Kühlkörpers eben ist, um das Metall zu einem ebenen, vorherrschend amorphen fortlaufenden Metallstreifen abzuschrecken, dadurch gekennzeichnet, daß die ebene Oberfläche des Kühlkörpers aus Molybdän besteht.

2. Verfahren nach Anspruch 1, das unter Vakuum mit einem absoluten Druck von weniger als 1 Inch Hg (3,4 kPa) durchgeführt wird.

3. Verfahren nach Anspruch 1 oder 2, worin das geschmolzene Metall eine Legierung ist, die ein oder mehrere hitzebeständige bzw. schwer schmelzbare Metalle enthält.

4. Vorrichtung zur Herstellung eines Metallstreifens direkt aus geschmolzenem Metall durch Auftreffenlassen des geschmolzenen Metalles auf die ebene Oberfläche eines sich schnell bewegenden Abkühlkörpers mit einem Abkühlkörper mit einer Oberfläche, die wenigstens in der Richtung quer zur Bewegungsrichtung des Abkühlkörpers eben ist, wobei diese Oberfläche so ausgebildet ist, daß sie geschmolzenes auf ihr auftreffendes Metall für ein rasches Abkühlen zum festen Zustand aufnimmt, und mit Einrichtungen, die funktionell mit dem Abkühlkörper zusammenwirken, um geschmolzenes Metall auf seiner Oberfläche auftreffen zu lassen, dadurch gekennzeichnet, daß die ebene Oberfläche des Abkühlkörpers aus Molybdän besteht.

5. Vorrichtung nach Anspruch 4, die in einer Vakuumkammer eingeschlossen ist.

6. Vorrichtung nach Anspruch 4 oder 5, worin der Abkühlkörper aus Kupfer besteht, das mit einer Abkühloberfläche aus Molybdän versehen ist.

7. Vorrichtung nach Anspruch 4, 5 oder 6, worin der Abkühlkörper eine ringförmige Abkühlwalze mit einer peripheren Abkühloberfläche aus Molybdän ist.

8. Vorrichtung nach Anspruch 4, 5 oder 6, worin der Abkühlkörper ein zylindrischer Abkühlkörper mit einer inneren Abkühloberfläche aus Molybdän ist.

FIG. 1

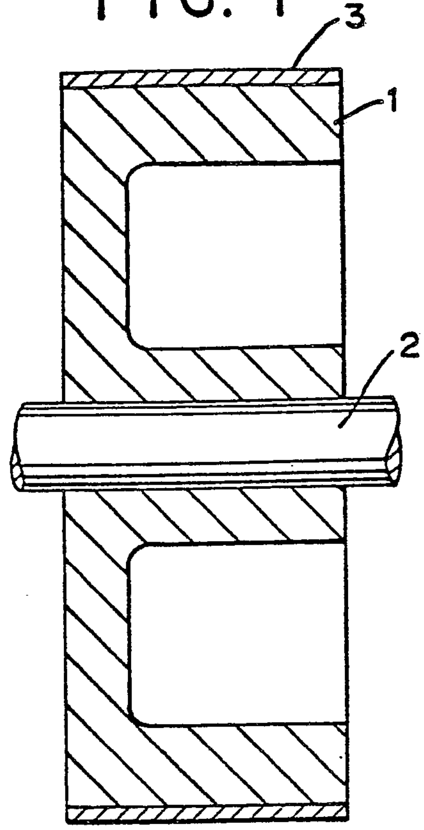
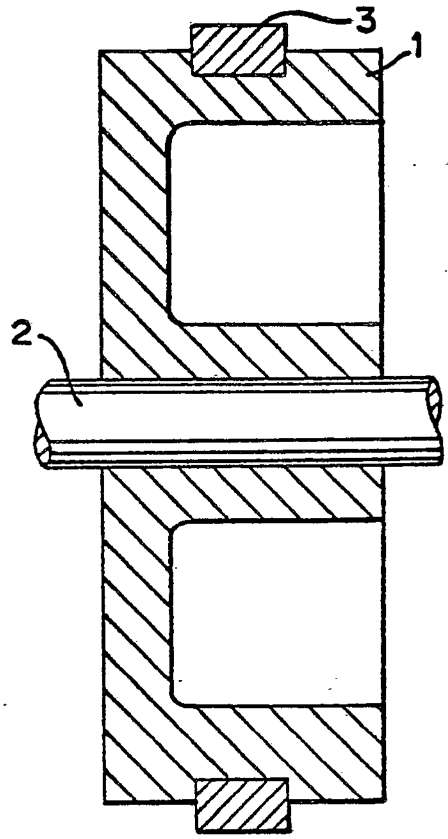


FIG. 2



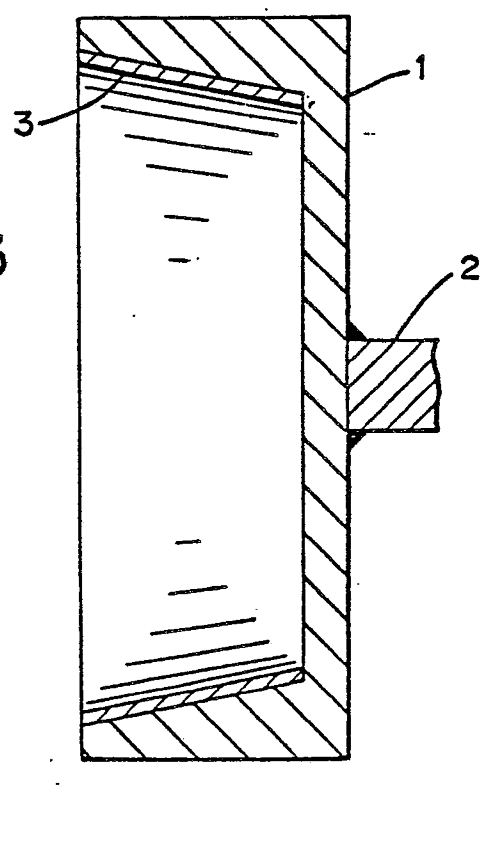


FIG. 3

FIG. 4

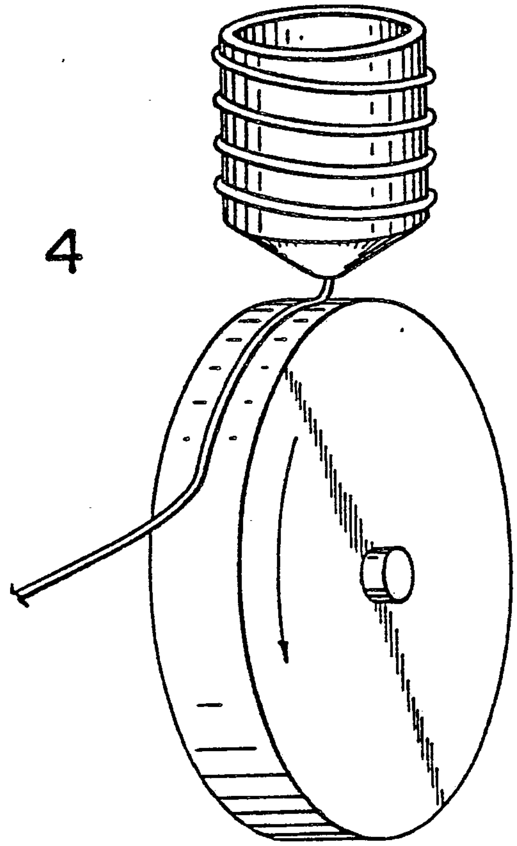


FIG. 5