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METHOD OF MAKING METAL FOILS

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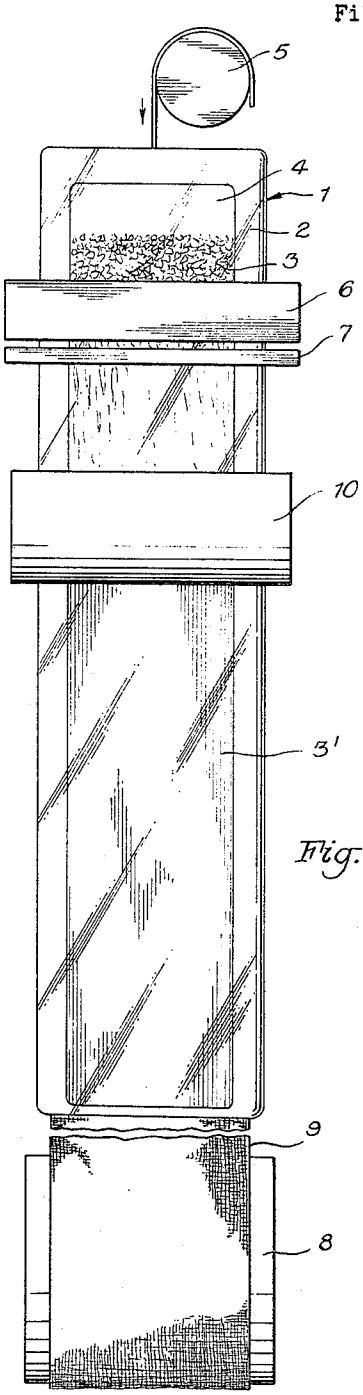


Fig. 1

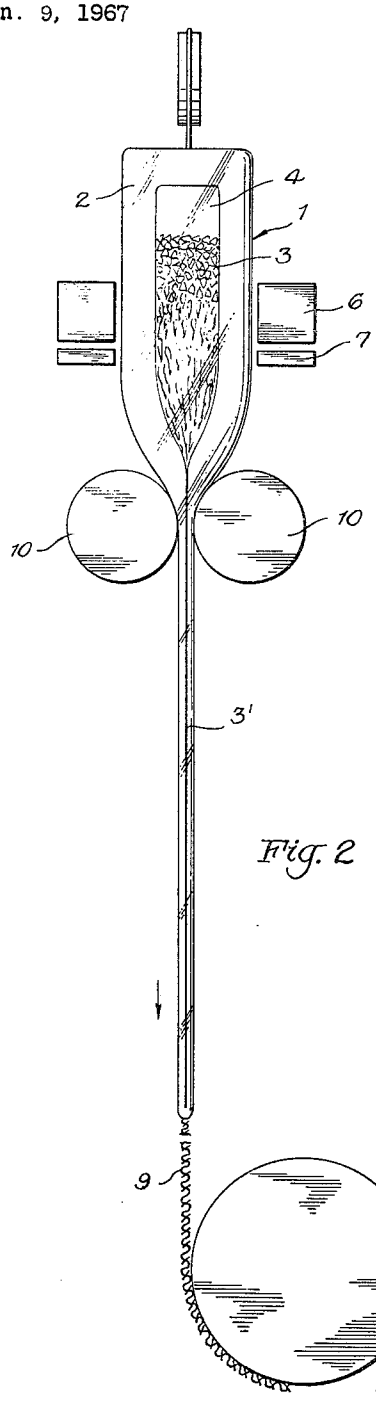


Fig. 2

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METHOD OF MAKING METAL FOILS

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ABSTRACT OF THE DISCLOSURE

A glass sleeve containing metal is heated until both glass and metal are plastic, and then elongated until the metal reaches foil thickness.

A method is known of making metal foils or thin metal strips down to about 5μ thickness by cold rolling or faggot rolling as the last shaping processes, preferably on multiple rolling mills with superimposed work rollers. This method involves additional expense through intermediate annealing treatments to eliminate cold-hardening which hamper or prevent the further processing stages, or also undesirable textures. Many materials, in particular heterogeneous alloys, which are characterised by two or several phases of different hardness and thus mostly varying plasticity at the same forming temperature, and also compound materials which in a metallic mass preferably contain non-metallic inclusions (dispersions) cannot be made at all, or if so, then only under aggravating conditions, such as the restriction to narrow rolling temperature ranges or small reductions per pass.

Thin metallic films are also made by methods of vacum vapor metallising or electro-deposition, by chemical reduction, by thermal decay of organometallic compounds on heated substances and by cathode pulverisation. But each of these methods has disadvantages which are a considerable hindrance to using the foils universally for technical requirements. Only mention here the unavoidable uneven porosity, especially in very thin films, unequal foil thickness, high internal tensions, inequalities of alloy composition caused by the method of manufacture, great surface roughness, expensive manufacturing techniques and control processes.

But all these disadvantages can be practically avoided if, in accordance with this invention, such foils and strips are made over the molten phase in a variation of the liquid-drawing method known for decades but restricted to the making of thin metal threads according to G. F. Taylor, in which the liquid metal is encased in a tough tube or sleeve of glass, quartz glass or Borax, and then drawn to many times its length and then after cooling the metal is exposed by etching off or dissolving the sleeve. It has also been proposed to draw simultaneously bundles or faggots of such wires with this or a related method, thus making μ thick wires of high strength.

This invention proceeds further with the perception that the achievement of optimal strength values in thin wires is practically limited by a wire diameter of 1 to 2μ, because only such wires can be controlled experimentally or in a production process; but it has been found that thin strips or foils with the same or even higher strength can be manufactured as equally sectioned threads and that in these the strip thickness or foil thickness can be greatly reduced in relation to the wire diameter while having equal or even better manageability, provided these foils and strips are given a work strip of much greater wall thickness which is separated by the end of the process.

The difficulties in the Taylor method with regard to material, method and cost have led to its not being used in production for some thirty years, and even in the last seven years it was only resumed experimentally when thin

wires were made as analogues to whiskers. The knowledge that the varying of this method could also bring great technical advance in the making of foils and strips was not available evidently because the field of manufacture of thin foils and strips in the range below 12μ was, as shown above, covered by relatively economic methods such as cold rolling with multi-roller mills, faggot-rolling the heating of gold foil of approx. 0.1μ thickness, on the other hand in the Angstrom and μ (=micrometer) range also by depositing methods, while for extremely thin wires in the range from 1 to 10μ no exchange method, e.g. by etching thicker wires, seemed technically equivalent.

A variation from the relatively expensive Taylor method and for thin strips and foils tolerating further difficulties of manufacture, was bound to imply overcoming a prejudice, insofar as an expert in the materials or the method, apart from the inventor, had throught of such a possibility at all. But only the years of occupation with the liquid-wire-drawing method according to Taylor and on the other hand the knowledge of the requirement for strips, foils and tube sections, and in particular those with the desired porosity and in alloys hard to form, especially for heavy-duty amouring, for fuel cells and microfilters and generally for special electronic and magnetic purposes—only all this experience led this inventor to recognize the secope inherent in the variation of the Taylor method from its application to threads to applying it to strips and foils. In addition, a number of other inventive ideas in this direction revealed not only the possible surprising, great technical advance, but also the economic practicability of the combined method thus achieved. In particular, the aspect was revealed that the liquid-drawing and rolling method in accordance with this invention always, through the inclusion in the program of tubes and shaped parts, indeed of massive strands on the one hand, and on the other through its applicability to normally brittle homogeneous or heterogeneous alloys and compound materials, became interesting also for greater material dimensions where a great reduction of wall thickness could be utilized in a single operation or where a directed solidification must be achieved.

A means by which some of theobjects of the invention are obtained are described with reference to the accompanying drawings, in which:

FIGURE 1 is a front elevational view of an apparatus schematically illustrating the method of this invention; and

FIGURE 2 is a side elevational view of FIGURE 1.

Compound body **1** is composed of a glass or quartz hollow shell or sleeve **2** having a metal filling **3** and at the upper end a vacuum or gas filled chamber **4**. Body **1** is slowly lowered by means of a pulley system **5**. In so doing, body **1** passes through a preheating zone **6** and is then heated in the melting-softening zone **7** until the glass sleeve and metal filling begin to flow. The flow speed is controlled by the draw-cylinder **8**, on which a pull strap **9** winds up, or by the calendar rollers **10** which may be driven. The strip of quartz or glass fabric **9** is fastened in advance by melting onto the lower edge of the compound body **1**. The formed metal material is the foil **3'**. The calendar rollers are preferably heat-resisting chrome-nickel-steel as is usual in making table glass. They can freely rotate, and in particular also be supported by other rollers. Their roller distance is continuously adjustable and where required electronically controlled for regulating the thickness of the metal strip or foil. Also in connection with thickness calibration of the foils and strips, the speed of the draw- and winding-in cylinders and the energy feed to the melting and softening zone can be electronically reverse-controlled. Instead of the

rollers or in addition, a flat guide nozzle, preferably narrowing downward, can also be used. Guide cylinders or rollers and nozzle can at the same time serve for cooling the shaped compound material. In addition, blowing or spraying devices can be used.

For the filling of the compound body, the suction of liquid metal and/or the insertion or introduction of premelted and pre-shaped metal plates have been found especially useful because they fill the space well. But also metal or alloy powder, metallic salts, threads, wires, foils, strips, shapes or mixtures of the same material, and in particular metallic whiskers can be put into the chamber oriented or disoriented, continuously or not, and also additives of non-metallic powders, especially inorganic whiskers, though having regard to the narrow melting zone they must be well mixed beforehand.

The hollow chamber accommodating the fillers can also be divided by inserted spacer pieces or profile rods, preferably melted to or adhering to the glass or quartz hollow sleeve, e.g. for the simultaneous making of several strips, and where necessary also of different metallic materials. In the same way, the glass or quartz distance plates need not be even or of equal thickness; they can have e.g. shaped grooves or ribs in the direction of draw provided for. On the other hand, it is also possible to use compound bodies divided by internal limiting plates of equal or different thicknesses so as to form a sandwich structure. It is often advantageous to have for the internal limiting plates and webs a glass material with a lower softening interval than that of the plates outside.

In another very important form of design of this invention, the manufacture of tubular bodies, the hollow glass or quartz body consists not of one sleeve but of a double-walled cylindrical body whose limiting walls are connected top and bottom by melted-on annular rings. For special fields of application, e.g. for making fuel cells, an arrangement of this is especially interesting in which the inside cylinder is disposed eccentrically to the outside one so that the metallic drawn body which forms is characterized by a continuously lessening and increasing wall thickness along the circumference. The drawn tubular glass-metal compound body is calibrated with the help of a guide nozzle which becomes smaller in the direction of draw and is preferably rotatable or oscillating, with a round or oval opening, which forms the strand from outside while it is still in the softening interval and/or with the help of a preferably rotatable or oscillating tongue or bolt which from above is passed through the melting and softening zone of the starting compound body and at least in this region consists of a highly heat-resistance ceramic or metallic material which then in the region of draw widens concentrically or asymmetrically, guiding and forming the tubular strand from the inside. With the aid of tongue and nozzle it is simultaneously possible, e.g. capacitively, to measure continuously the thickness of the drawn metal tube, and thus to regulate the velocity of draw electronically on the one hand, but also, provided tongue and nozzle are disposed conically differentially in their opposing work surfaces and mutually adjustably in the direction of draw, preferably over the minimum distance to control direct tube diameter and wall thickness.

This invention also comprises the widening of the draw compound tube beyond the dimensions of the starting body to a given dimension by using the tongue without the nozzle, and the making of in themselves conical tube sections by lateral displacement of the tongue to a pre-set program. The tongue can be perforated and have one or several cooling pipes for self-cooling and for cooling the inside of the drawn compound pipe and thus for quenching the metal tube drawn to a thinner wall thickness. Where it has a rotationally symmetrical form and is disposed centrally, it can slide continuously over the entire inside surface of the drawn compound tube; disposed as an excentric disk and/or asymmetrically shaped, the tongue, provided rotation is rapid enough around an axis parallel to the direction of draw, touches the drawn compound tube only on a screw-thread line or screw surface.

Accordingly the nozzle also can have holes for outside cooling and on its part perform rotations not only round the symmetrical axis of the drawn compound tube but as an eccentric ring also round an axis parallel thereto, thus sliding symmetrically over the entire outside surface of the tube, or else touch it only along a screw-thread line or screw surface. Preferably excentric ring and disk should work at the same elevation and be driven separately from outside and inside.

Just as in liquid drawing of strips, foils and shapes, this invention includes for liquid tube drawing the insertion of spacer pieces and shape strips softening preferably at lower temperatures and the use of grooved and ribbed cylindrical outside and inside bodies of the same or different sorts of glass. This enables a greater number of wires with any desired section to be drawn simultaneously. On the other hand, it is possible by appropriately designing the hollow chambers to provide solid or glass-filled metallic work strips for single or several strips, foils or shape strips and tubes to be made, which work strips facilitate the holding or management of the end products, especially those with very thin walls, and where necessary can be worked off subsequently or be used still as conductors.

For making compound products a special provision is the introduction of very this, preferably slotted or perforated intermediate shapes or plates of glass which in the drawing and rolling process preferably unite with the other glass material but allow the welding of different metals or alloys introduced as solid bodies on both sides of the shapes.

It has proved of special advantage to adapt the compositions of the various glass plates and shapes to the composition of the metals and alloys to be drawn that softening and melting intervals approximate to each other so that the viscosity of the outside limiting plates or tubes is greater than or equal to the viscosity of any inside limiting plates, tubes or shapes in glass or quartz glass, but in any case greater than the viscosity of the liquid or doughy metallic phase with or without solid portions. But it is also possible with the method in accordance with the invention to process especially high melting metals such as niobium, tantalum, zirconium and their alloys by using appropriately regulated and rapid energy feeding to heat the metallic portions beyond their melting points to far higher temperatures than the surrounding glass materials. In particular, this has revealed that very rapid heating and rapid cooling in liquid drawing and rolling allows reactions between metal and glass, in particular the absorption of silicon from the glass, to be avoided. An important factor for this is that the hollow spaces remaining between glass and metal in the initial compound body be evacuated before melting begins and where necessary currently during liquid drawing.

The compound body can be heated to liquefaction at will by heat radiation or inductive heating or also by electronic, plasma or Laser radiation or by simultaneous use of several forms of heating. The required reduction of wall thickness can be done in one or several heatings of the compound body or of the intermediate products. Very big pass reductions, e.g. in the ratio 1000:1 are advantageous for very thin and long foils and strips, e.g. a reduction of the metallic wall thickness from 1 mm. to 1μ, when the foils or strips are wound on the draw cylinder. On thes other hand in making tubes and, particularly, conical tube sections of greater diameter and also e.g. foils and strips with about 50μ to 1 mm. wall thickness of brittle alloys shorter work lengths and correspondingly smaller pass reductions will be accepted and lower draw velocities will be used. These details

show already the possible scope of performance of a single liquid drawing and rolling plant, a performance which can be achieved by relatively simple reconstruction and alterations of adjustment.

The characteristics of this invention also include the cooling of the drawn or rolled compound foils, strips, tubes or shapes, immediately after the forming process with such a speed of high temperatures, by blowing or spraying that according to the composition of the metallic material portion those conditions of balance or deep cooling are obtained which are a requirement for achieving especially favorable chamical or physical properties, without or with a subsequent heat treatment. The drawing or rolling process with subsequent cooling operation can also be performed where required in its last phases so that partial forming of the metallic or metallic-ceramic phases occur in the solid state and these thus receive a texture. It is even possible that the final forming is done at such low temperatures of the metallic component that cold work-hardening may occur in them.

In particular, it has also been found advantageous for compound tubes made in accordance with the invention further to be slotted and then flat rolled lengthwise for making foils and strips directly following the drawing operation.

The steps in the method described are preferably performed in a vertical or oblique working direction, but it is often favorable to provide according to the greatest sectional reduction of the viscous-drawn meterial a guide roller or ways in the horizontal work direction with additional heating of the material where required.

The drawn and rolled material obtained in accordance with this invention can be used immediately or after subdividing as compound material with adhering or interspersed layers of glass, e.g. for condensers and razor blades. But these layers can also be detached on one or all sides. The complete or partial detachment is done in a manner itself known by mechanical means e.g. by cutting, grinding, bursting or radiation under the influence of heat tensions or by chemical means e.g. in hydrofluoric acid or a bath selected in accordance with the composition of the glass, more especially a molten salt bath, or by a combination of these methods. One appropriate method where the end stage is required to consist of metal parts with a glass coating on one side is to start the drawing operation of glass-metal compound bodies with particularly thick glass plates on one side and then to etch off the finally obtained compound material only so far that on one side a glass or quartz layer remains on the metallic material. One special type of method in making tubular foils provides for the liquid or gaseous coolant fed through the drilled tongue to be supplemented by metallic or ceramic powder to enhance the cooling or for the immediate manufacture of compound products, in some cases also chemicals which attack the inside skin of glass.

Experience shows that, according to the steps of the method described above, the metallic material, because of being made over the liquid state, occurs in the form of dense foils, strips, tubes or shapes, unless because of its composition according to the laws of heterogeneous equilibrium a gaseous phase forms after solidifying and exudes, which especially in very thin-walled bodies itself causes porosity. Otherwise in the foils and tubes made in accordance with this invention there are not only the known methods of technical aid, such as mechanical perforation, slotting, electro-erosive processing with the spark, the electronic ray, the palsma ray or the Laser ray, but especially the possibilities of chemical or electromechanical elimination of a metallic or non-metallic phase finely distributed in the basic metallic mass.

The resulting holes can be subsequently widened by mechanical means, e.g. by rolling or drawing, as e.g. in so-called expanded metal, or else narrowed by e.g. cold pressing or vaporising or additional electrolytic or chemical deposition.

Also the application of several of these methods simultaneously can in accordance with the invention mean an extraordinary technical advance.

One special form of design for making metallic capillary filters is now described. The initial glass-metal compound body is constructed so that outside, as described above, thicker glass or quartz plates or a corresponding tube are disposed, but in the hollow space in the intended direction of draw a system of glass rods, which are mutually separated by the initial metallic materials, is disposed. After performing the drawing process the strands obtained are cut to the required capillary length, e.g. with a microtome, and the glass mass etched off or out. It is often appropriate first to free the resulting strands only from the outside glass mass, to weld or solder them closely together in suitable lengths, and only then to cut the larger cross-sections with the microtome and do the etching. The filters thus obtained are especially suitable as electrodes for fuel cells; the welds serve in this case preferably as conductors—unless first provision was made in the initial glass-metal compound body for conduction with substantial metallic glass-free areas.

But in the above described hollow space, a system of glass or quartz tubes can also be accommodated, the interstices filled with fritted glass, but the tubes themselves with metal, and after the drawing process and cutting with the mricotome the metal eliminated, thus making glass filters of even porosity.

Another form of design for fuel cell electrodes is obtained when in the hollow space of the initial quartz hollow sleeve or cylinder e.g. a mixture of platinum powder with fine magnesium oxide is introduced, filtered first to an even grain size and particularly containing no oversize grains. By liquid drawing with the metallic material at temperatures around 1,900° C., a foil or tubular foil is made of a thickness corresponding to the grain size of the magnesium oxide. The magnesium oxide grains are then largely evenly, according to the previous mixing, distributed in the platinum foil and reach on both sides into the areas of contact. By etching off the quartz-glass skin and etching out the magnesium oxide grains, relatively evenly porous platinum foils are obtained.

Naturally it is possible by pressing together such foils with different-sized pore diameters to make double or multi-layer electrodes characterized by particularly low weight.

Metal foils glass insulated on both sides are suitable for e.g. razor blades. The metal foil serves as a tough carrier body, the glass edge protruding along the direction of draw as the cutting edge. For making glass-insulated foils it can be advantageous to work to an appropriately varied liquid faggot-drawing or rolling method in which the hollow space of the initial body is divided up by a large number of parallel glass plates. Alternately between these glass plates metal pates or powder from the intended foil metal and a preferably low-melting auxiliary metal or an alloy of other composition is introduced so that these metals do not come into contact with each other. After removing the outside glass skin, thin glass-insulated metal foils are easily obtainable on both sides by fusing or chemical or electrolytic dissolution of the auxiliary metal.

Metal foils made in accordance with the invention differ from those in accordance with the known methods, e.g. by vaporization, particularly by their great evenness of surface, their high degree of freedom from stress, but also by the more even lattice structure. Thus it is e.g. possible to make metallic monocrystal foils or metal-quartz foil combinations in which the quartz foils also have monocrystal character. It should be emphasized here that it is also possible with the method in accordance with the invention to make magnetic foils in thicknesses

up to several hundred Angstrom units which in electronic storing instruments respond in the nanoseconds range.

No claim to completeness is made for the following list of further possible applications of objects made in accordance with the invention, taking as a starting point heterogeneous or homogeneous or compound materials compacted by pressing or shock-wave (explosive) forming, in particular coated materials and/or objects with foil structure as highly heat-resistant parts in place of fiber materials. For this, parts with thin glass and quartz inlays can often be used with advantage, particularly when they are initially made as stratified materials and perforated intermediate glass plates initially allowed local connecting ribs to form between the metal layers in the initial compound body. According to the foil thickness, single foils and compound bodies, in particular plated, twisted and woven strips can serve as superfirm metal inlays for armouring purposes. Objects made in accordance with the invention are also highly suitable as catalysts and and catalyst agents for artificial denture parts, soldered shapes, for making printed circuits, as selenium strata for electrostatic copying devices, for supraconductive coils, conductive suspensions, for thermo-elements and thermopiles, as bimetals, capacitors, contacts, high-ohmic resistors, counter tubes, control and storage elements, planar transistors, and generally for active and passive electronic components. The method described also allows the making of novel magnetic special materials, especially with foil thicknesses in the range of some hundred and thousand Angstrom units with glass or quartz foil as antimagnetic agents, and also massive permanent-magnetic strands with crystal orientation in the direction of draw, additive materials for textiles or for metallizing and cheap manufacture of plating materials, e.g. gold leaf. The scope of application for optical and electro-optical purposes must also not be forgotten, for mirrors, reflectors, light diffusers, optic light filters and anti-radiation coatings, photocells, rectifiers, large-area solar cells, large-area lighting fixtures (carpets) with high energy exploitation, polarizable surfaces, windows for soft X-rays and electronic rays, targets. It would go too far to adduce proof all advances attainable and attained with the new method of this invention.

Having now described the means by which the objects of this invention are obtained, I claim:

1. A method of making a metal foil comprising introducing the metal into a glass sleeve, heating the sleeve and metal to a temperature at which they have a plastic flow, elongating and flattening the heated sleeve and metal by drawing until the metal has a foil thickness, said sleeve maintaining the shape of the foil being formed, cooling the glass sleeve and metal, and then removing the glass sleeve to expose the metal foil.

2. A method as in claim 1 in which the sleeve and metal are flattened by being drawn vertically downwards to decrease the thickness of the sleeve and metal.

3. A method as in claim 1, said sleeve and metal being flattened by thinning the walls of a double wall hollow sleeve to form a tubular foil.

4. A method as in claim 3, further comprising eccentrically forming one wall of said double wall by use of an eccentric ring and disk.

5. A method as in claim 1, further comprising a metal composed of a group of fine metal fibers for forming a foil filter.

6. A method as in claim 5, further comprising glass fibers dispersed between said metallic fibers.

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