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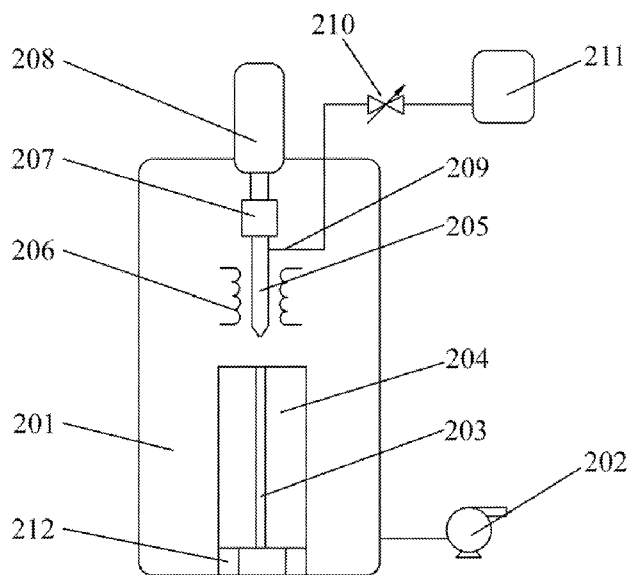


Fig.2

(57) Abstract: A method for fabricating a  
bulk metallic glass tube (303), the tube fab-  
ricated and a coriolis flowmeter equipped  
with the tube are disclosed. The method  
comprises: a) melting an alloying material  
capable of yielding an amorphous alloy in a  
melting vessel (205); and b) injecting the  
resultant molten alloying material into a  
through-hole mold channel (203), of which  
the surface is coated with a demoulding  
agent, of a forced cooling casting mold (204)  
through the pressure difference between two  
ends of the molten alloying material, so that  
the molten alloying material in contact with  
the surface of the mold channel (203) is then  
rapidly cooled down to below its melting  
point while the molten alloying material at  
the center of the mold channel (203) still  
maintains a liquid state and flows forward  
continuously, leading to the formation of the  
tube. With this method, there's no need to in-  
sert a mold core in the mold channel (203),  
and the length and the thinness of the wall of  
the obtained bulk metallic glass tube (303)  
can be improved.

## **Method and Apparatus for Fabricating Bulk Metallic Glass Tube, Tube Fabricated and Coriolis Flowmeter Equipped with the Tube**

### **Field of the Invention**

The present invention generally relates to a method for fabricating a bulk metallic glass tube, and more particularly relates to a mould casting method for fabricating a bulk metallic glass tube.

### **Description of the Prior Art**

Metallic glass is a metallic material with a disordered atomic-scale structure. Materials with such disordered structures are created directly from the liquid state during cooling. However, the rapid cooling rate, occurring at millions of degrees a second, is too fast to manipulate for mass production of the materials. More recently a number of alloys with critical cooling rates low enough to allow formation of amorphous structure in thick layers (over 1 millimeter) have been produced, these are known as bulk metallic glasses (BMG).

An attractive family of bulk metallic glass alloys may be described by the molecular equation:  $Ti_a Zr_b Cu_c Ni_d Al_e Si_f Hf_g$ , where  $a$  has a ratio that is in the range of 0 to 50,  $b$  has a ratio that is in the range of 0 to 60,  $c$  has a ratio that is in the range of 0 to 50,  $d$  has a ratio that is in the range of 0 to 10,  $e$  has a ratio that is in the range of 0 to 15,  $f$  has a ratio that is in the range of 0 to 3 and  $g$  has a ratio that is in the range of 0 to 5. The excellent properties of this family of materials, such as ultrahigh strength, large elastic elongation, low Young's modulus, high corrosion resistance and good soft magnetic properties, make them promising for industrial products. For example, in the coriolis mass flowmeter, the sensing tube that is made of this kind of amorphous alloys has been proved to provide high sensitivity measurement and a high pressure threshold (Chaoli Maa, Nobuyuki Nishiyama, Akihisa Inoue. Fabrication and characterization of Coriolis mass flowmeter made from Ti-based glassy tubes. Materials Science and Engineering A 407 (2005) 201–206).

In the field of coriolis flow meter, the highly sensitive and strong flow meter tube is required to replace the traditional sensing tube made of stainless steel for precise measurement of ultralow flow in all pressure environments. The excellent mechanical and anticorrosion

properties of bulk metallic glass represent an opportunity for such requirements.

In the commercial coriolis mass flow meter, the sensing tube should be very thin and be normally designed as U-shape or S-shape, which is bended from a straight tube. So, the primarily straight tube needs to be thin and long enough. Furthermore, the tolerance of the tube wall thickness should be low to guarantee the consistency of the measured signals from different positions of the tube.

Unfortunately, the traditional fabrication process for stainless steel tubes is not suitable for making bulk metallic glass tube. For example, cold draw is a metalworking process which uses the plastic deformation of the metal in the room temperature to make wires, bars and tubes. The starting stock (tube) is drawn through a die to decrease its diameter, increase its length and improve dimensional accuracy. But, the plasticity of the metallic glass in the room temperature is very low and is not suitable for processing by cold draw. Another traditional method is to make a welded pipe, which is formed by rolling a plate and welding the seam. But, it is difficult to keep the amorphous structure of the metallic glass tube because it will crystallize during the heating process. Based on the forming mechanism of bulk metallic glass, the casting technique is the most reasonable solution. There are some researches to attempt to fabricate the metallic glass tube. However, the molten alloy is so viscous that its low flowability prohibits it from filling up the narrow space in the mold. Consequently, it is very challenging to cast such a long and thin tube.

CN 101036943 proposed a method for producing a non-crystal alloy tube. A mold core is inserted into the mold and the molten alloy is filled in the interspaces between the mold core and mold. So, the tube shape is controlled by both the mold and mold core. However the proposed solution has two main problems. Firstly, it is difficult to fill the viscous molten alloy in the narrow space between the mold and mold core, which prohibits thinness and uniformity of the tube. The wall thickness of the tube based on the method is normally above 2 mm. Secondly, if the required tube is long, then it is difficult to remove the mold core without damaging the tube.

In order to make a thin tube suitable for a coriolis flow meter, a research team in Japan re-engineers suction casting process by simultaneously filling and solidifying the material in the mold to eliminate the use of the mold core. JP2000271730 disclosed an equipment to make a Ti-based glassy alloy tube. The equipment consists of a carbon crucible, a mobile pipe-shape

copper mold and a water-cooling system. The alloy ingot in the crucible is first induction heated to above the melting point and then the mobile copper mold is pushed down into the melted metal to certain depth. At the same time, a negative pressure is applied at the other end of the mobile copper mold and instantaneously the melted metal is sucked up into the copper mold. The melted alloy that is in contact with the mold surface is then rapidly cooled down to below the melting point and starts to solidify. Meanwhile, the temperature of the melted metal at the center of the mold is still high and the temperature gradient sustains continuous movement of the melted metal, leading to the formation of a tube. However, tubes made from the method are not long enough, for example, only between 100 mm and 200 mm. Because the relatively high viscosity of the molten alloy affects its flowability in the copper mold, the solidification of the whole molten alloy at the top point prevents it from flowing upward.

CN 101774009A discloses a device and a method for shaping an amorphous alloy tube. The device is a shaping device with a mold cavity, which is formed by the assembly of an arc-melting furnace, a copper crucible, a temperature measuring device, a suction casting valve, a mechanical pump, a tungsten electrode, a metal mold, a suction casting controller and a melting current controller. The method comprises the following steps: an alloy ingot is input; the vacuum degree is  $5.0 \times 10^{-3}$  -  $6.0 \times 10^{-3}$  Pa; the melting current is 250-400A; and when the bottom temperature of the alloy ingot is more than the liquid-phase temperature, the suction casting controller opens the suction casting valve, the mechanical pump draws the air out of the inner cavity of the arc-melting furnace, the alloy liquid flows into the mold cavity, the alloy liquid in contact with the side wall of the mold cavity forms a very thin metal scull on the side wall of the mold cavity, and the unsolidified alloy liquid in the center is drawn out of the mold. The invention is used for shaping of the slim alloy tube. However, the tube formed by this method is not very satisfactory, because the length of the formed tube is still not long enough. Though the length of the mold is 200-300mm, the length of the tube formed is very difficult to exceed 250mm. In addition, the wall thickness is also not consistent along the whole tube.

Up to now, there is no solution that can fabricate a thin and long bulk metallic glass tube, especially a bulk metallic glass tube longer than 300mm. Therefore, a new solution is required.

### **Summary of the invention**

Accordingly, the present application has been made to address the requirement for such a new solution.

One object to be achieved by the present invention is to provide a novel fabricating method of bulk metallic glass tube. With this method, there's no need to insert a mold core in the mold channel, and the length and the thinness of the wall of the obtained bulk metallic glass tube can be improved.

Further object of the present invention is to provide an apparatus for fabricating bulk metallic glass tube.

Another object of the present invention is to provide a thin and long bulk metallic glass tube fabricated by the novel fabricating method. The length of the bulk metallic glass tube can be longer than 300mm, which can not be realized in the prior art. Such a bulk metallic glass tube is long enough to replace the stainless steel tube in a coriolis flow meter.

Yet another object of the present invention is to provide a coriolis flow meter equipped with the bulk metallic tube of the present invention.

To accomplish the objects described above, according to the first aspect of the present invention, there is provided a method for fabricating a bulk metallic glass tube comprising the steps of:

a) melting an alloying material capable of yielding an amorphous alloy in a melting vessel;  
and

b) forcibly injecting the resultant molten alloying material into a through-hole mold channel of a forced cooling casting mold through the pressure difference between two ends of the molten alloying material, so that the molten alloying material in contact with the surface of the mold channel is then rapidly cooled down to below its melting point while the molten alloying material at the center of the mold channel still maintains a liquid state and flows forward continuously, leading to the formation of the tube, wherein the through-hole mold channel of the casting mold is coated with a demoulding agent.

The applicant of the present invention surprisingly finds that through coating the demoulding agent on the mold channel surface, the flowability of the molten alloying material can be dramatically improved which is advantage to form a tube, especially to form a longer and thinner tube. Without being bound by theory, it is believed that the demoulding agent between

the molten alloying material and the casting mold can further block the heat transfer and reduce the solidification speed. So the molten alloying material at the center of the mold channel can flow more fluently, which leads to the formation of a thinner and longer tube.

Preferably, the demoulding agent is chosen from a demoulding agent that can form a film on the surface of the through-hole mold channel when being applied thereto. The film formed by a demoulding agent on the surface of the mold channel can benefit for the formation of a smooth outer surface of the tube. Further, due to the formation of the film of the demoulding agent, the surface of the mold channel is smoother and the molten alloying material can flow more easily and thus a longer tube can be formed.

Preferably, the demoulding agent is chosen from a demoulding agent of emulsion type. More preferably, the demoulding agent is chosen from boron nitride emulsion and molybdenum disulfide emulsion.

Preferably, the molten alloying material is injected under a continuous pressure of a compressed gas. Since the molten alloying material is continuously pressured by the compressed gas, less molten alloying material will be cooled and solidified, while more molten alloying material at the center of the mold channel still maintains a liquid state and flows continuously under the pressure of the compressed gas, leading to the formation of a thinner and longer tube.

In a preferred embodiment, the steps of a) and/or b) are carried out in a vacuum or under an atmosphere of inert gas, so as to prohibit the oxidation of the molten alloying material. Preferably, the step of b) is carried out in a vacuum. The vacuum can provide higher pressure difference between two ends of the molten alloying material and improve the injection speed of the molten alloying material so as to facilitate the formation of tube. Specifically, the melting vessel and the casting mold are enclosed in an enclosure space, and the enclosure space is vacuumed before the step of b). Since the enclosure space is vacuumed, the molten alloying material may not be easily oxidized. Further, the vacuumed enclosure space can provide higher pressure difference between two ends of the molten alloying material and improve the injection speed of the molten alloying material so as to facilitate the formation of tube, especially the formation of a longer tube.

In order to obtain a thin and homogenous tube, it is preferable that the method of the present invention further includes the step of: c) utilizing low-speed wire electrical discharge machining

to reshape the tube obtained by b). Specifically, the tube obtained by the step of b) is fixed by a clamp, a thin brass wire is fed through the tube and is controlled by CNC (Computer Numerical Control) to move inside the tube, and then the thick parts of the tube will be removed by the sparking from the sides of the wire to the tube. In order to decrease the effects of the heat generated from the process, the whole tube is submerged in a tank of dielectric fluid, which is typically deionized water. In the low-speed wire electrical discharge machining process, the wall thickness and the tolerance of the outer diameter and inner diameter can be easily guaranteed by the CNC-based control.

In order to eliminate the possible surface defects caused by the low-speed wire electrical discharge machining, it is further preferable that the method of the present invention further includes the step of: d) electropolishing the tube obtained by step of c). Specifically, the tube obtained by the step of c) should be immersed in the electrolyte and connected to the electrode with DC power. The rough portion on the tube surface will be oxidized and dissolved in the electrolyte. Finally, a long, thin and homogenous bulk metallic glass tube is obtained.

In the method of the present invention, the composition of the alloying material can be chosen and determined according to the practical application of the tube. The shape of the tube, including its length, outer diameter and inner diameter and etc, can be controlled by adjusting the parameters in the process of the method. For example, when injecting the molten alloying material, increasing the pressure difference between two ends of the molten alloying material and/or increasing the melt temperature of the molten alloying material will be helpful for forming a longer and thinner tube. Increasing the pressure difference between two ends of the molten alloying material may be realized through increasing the pressure of the compressed gas and/or the vacuum degree of the enclosure space.

In accordance with the second object of the present invention, there is provided an apparatus for fabricating a bulk metallic glass tube including:

- i) a melting vessel for containing an alloying material capable of yielding an amorphous alloy;
- ii) a heater for heating and melting the alloying material contained in the melting vessel;
- iii) a pressure difference generator for producing a pressure difference between two ends of the molten alloying material contained in the melting vessel;

iv) a forced cooling casting mold provided with a through-hole mold channel coated with a demoulding agent.

Preferably, the demoulding agent is chosen from a demoulding agent that can form a film on the surface of the through-hole mold channel when being applied thereto.

Preferably, the demoulding agent is chosen from a demoulding agent of emulsion type. More preferably, the demoulding agent is chosen from boron nitride emulsion and molybdenum disulfide emulsion.

Preferably, the pressure difference generator includes a gas container filled with a compressed gas, said gas container is connected to the melting vessel through a gas conduit controlled by a valve.

Preferably, the apparatus for fabricating a bulk metallic glass tube further comprises a chamber connected to a vacuum pump, the melting vessel, the heater and the casting mold are enclosed in the chamber.

Preferably, the apparatus for fabricating a bulk metallic glass tube further includes a clamp and a mover, the melting vessel is fixed by the clamp, the mover is connected to the clamp for adjusting the position of the melting vessel.

In accordance with the third object of the present invention, there is provided a bulk metallic glass tube fabricated by the fabricating method of the present invention, wherein the length of the bulk metallic glass tube is longer than 300mm.

Preferably, the wall thickness of the bulk metallic glass tube is from 0.1mm to 0.25mm.

Preferably, the tolerance of the outer diameter and inner diameter of the bulk metallic glass tube is within  $\pm 0.01$ mm.

Preferably, the bulk metallic glass tube is a Ti-based bulk metallic glass tube.

In accordance with the fourth object of the present invention, there is provided a coriolis flow meter equipped with at least one bulk metallic glass tube of the present invention as the sensing tube. The bulk metallic glass tube of the present invention is long enough to be used in the flow meter to replace the traditional stainless steel tube. When comparing with the traditional stainless steel tube, the bulk metallic glass tube has superior strength, lower Young's modulus and higher corrosion resistance. So the flow meter equipped with the bulk metallic glass tube of the present invention can be used in various corrosive fluid and all pressure environment. In



addition, the wall thickness of the bulk metallic glass tube can be controlled to be very thin, for example, 0.1-0.25 mm, it is able to reduce the thickness of the sensing tube of the flow meter. Further, the tolerance of the bulk metallic glass tube of the present invention is within  $\pm 0.01$  mm, the sensitivity and accuracy of the flow meter can be guaranteed and improved.

### **Brief Description of the Drawings**

The above and other objects, features and advantages of the present invention will be more apparent from the following detailed description taken in conjunction with the accompanying drawings, in which:

Fig. 1 is a flow chart of the method for fabricating a bulk metallic glass tube according to one embodiment of the present invention;

Fig. 2 is a schematic diagram of the apparatus for performing the vacuum injection casting of Fig. 1;

Fig. 3 is a photo illustrating several samples of Ti-based metallic glass tube fabricated by the apparatus shown in Fig. 2; and

Fig. 4 is a schematic diagram of the configuration of Low-speed wire electrical discharge machining.

### **Listing of Reference Signs**

201 chamber	202 vacuum pump
203 Mold channel	204 casting mold
205 Melting vessel	206 heater
207 clamp	208 mover
209 Gas conduit	210 valve
211 Gas container	301 tube clamp
302 Brass wire	303 tube

### **Detailed description of the invention**

Hereinafter, a preferred embodiment of the present invention will be described with reference to the accompanying drawings. The matters defined in the description, such as the detailed construction and elements, are nothing but specific details provided to assist those of

ordinary skill in the art in a comprehensive understanding of the invention, and thus the present invention is not limited thereto.

Fig. 1 is a flow chart of the method for fabricating a bulk metallic glass tube according to one embodiment of the present invention.

In step 101, the vacuum injection casting is performed. Specifically, an alloying material capable of yielding an amorphous alloy is melted in a melting vessel, and then is forcibly injected into a through-hole mold channel of a forced cooling casting mold through the pressure difference between two ends of the molten alloying material, so that the molten alloying material in contact with the surface of the mold channel is then rapidly cooled down to below its melting point while the molten alloying material at the center of the mold channel still maintains a liquid state and flows forward continuously, leading to the formation of the bulk metallic glass tube, wherein the through-hole mold channel of the casting mold is coated with a demoulding agent.

Fig. 2 is a schematic diagram of the apparatus for performing the vacuum injection casting of Fig. 1. The apparatus comprises a chamber 201 that can be vacuumed by a vacuum pump 202. A heater 206, a melting vessel 205 and a casting mold 204 provided with a casting channel 203 are enclosed in the chamber 201. The casting mold 204 is supported by a cushion block 212, leaving the lower end of the casting channel 203 unblocked. The melting vessel 205 is fixed by a clamp 207. A mechanical mover 208 connected to the clamp 207 can adjust the position of the melting vessel 205 freely. The melting vessel 205 is connected to a gas container 211 filled with a compressed gas through a gas conduit 209. The open and close of the gas conduit 209 is controlled by a valve 210. The gas container 211 filled with compressed gas maintains enough pressure difference between two ends of the valve 210. Once the valve 210 is opened, the high pressure gas flow can inject the molten alloying material into the mold channel 203 with high speed.

The alloying material powder is placed into the melting vessel 205. In this embodiment, the melting vessel 205 is a quartz tube with a nozzle. The diameter of the quartz tube nozzle is 1.2 mm. In order to prevent the alloying material powder from leaking out of the quartz tube, the particle size of the alloying material powder should be larger than the nozzle diameter of the quartz tube.

Before melting the alloying material powder in the melting vessel 205, align the melting

vessel 205 with the casting mold 204 manually. When manually aligning the melting vessel 205 and casting mold 204 with proper contact angle and force, the apparatus can remember the set position and auto-align at injection. That is to say, at the beginning of the casting, the mover 208 moves up and the melting vessel 205 is in the middle of the heater 206. When the alloying material powder in the melting vessel 205 is induction heated and melted by the heater 206, the mover 208 moves down to the set position where the quartz tube nozzle is exactly contacted with the mold gate as a manual operation. Then the valve 210 is opened and the molten alloying material is pushed by the gas flow from the gas container 211 filled with the compressed gas through the gas conduit 209 and injected into the mold channel 203 of the casting mold 204. The molten alloying material in contact with the surface of the mold channel 203 is then rapidly cooled down to below its melting point and solidified immediately. Meanwhile, the temperature of the molten alloying material at the center of the mold channel 203 is still high and maintains a liquid state. The temperature gradient sustains continuous movement of the molten alloying material, leading to the formation of a bulk metallic glass tube.

In order to obtain a longer tube, a demoulding agent is coated onto the surface of the mold channel 203. The demoulding agent may be chosen from a demoulding agent of emulsion type such as boron nitride emulsion, molybdenum disulfide emulsion and the like. By coating the demoulding agent on the mold surface, the flowability of the molten alloy is dramatically improved. In addition, the demoulding agent between the molten alloy and the mold can block the heat transfer and reduce the solidification speed. Finally, the tube with more than 300 mm length can be fabricated by the vacuum injection casting process.

Fig.3 shows some tube samples fabricated from the vacuum injection casting process. The outer diameters of the three samples are respectively 2mm, 3mm and 4mm and the lengths of them are all above 300 mm.

In a preferred example, in order to prohibit the oxidation of the molten alloy, before melting the alloying material powder in the melting vessel 206, the chamber 201 is vacuumed by the pump 202. Further, the vacuum can provide higher pressure difference between two ends of the molten alloying material and improve the injection speed of the molten alloying material so as to facilitate the formation of thinner and longer tube.

Alternatively, the step of melting the alloying material may also be performed under an

atmosphere of inert gas, so as to prohibit the oxidation of the molten alloying material.

In a preferred example, in order to improve the uniformity of the inner diameter of the tube obtained by the step 101, the step 102 of low-speed wire electrical discharge machining is further included. Low-speed wire electrical discharge machining is utilized to reshape the tube. As can be seen from fig. 4, the tube 303 obtained by the step 101 is fixed by a tube clamp 301. A thin brass wire 302 is fed through the tube and is CNC-controlled to move inside the tube. The thick parts of the tube will be removed by the electrical sparking from the thin brass wire 302 at the work piece. In order to decrease the effects of the heat generated from the process, the whole work piece is submerged in a tank of dielectric fluid, which is typically deionized water. After this step, the tube with symmetrical wall thickness can be obtained.

In order to eliminate the possible surface defects caused by the step 102, in the further preferred example, the step 103 of electropolishing is further included. In the step 103, the tube should be immersed in the electrolyte and connected to the electrode with DC power. The rough portion on the tube surface will be oxidized and dissolved in the electrolyte. Finally, a long, thin and homogenous bulk metallic glass tube is obtained.

The wall thickness of the bulk metallic glass tube fabricated according to the method of the present invention can be controlled to be from 0.1mm to 0.25mm and the tolerance of the outer diameter and inner diameter can be controlled to be within  $\pm 0.01$ mm.

Hereinafter, several examples will be described, wherein examples 1-3 are performed in the apparatus shown in fig. 2, and the examples 4-5 are carried out on the tubes obtained from examples 2-3, respectively, according to the steps 102-103 shown in fig. 1.

#### Example 1

Align the melting vessel 205 with the casting mold 204 manually. When manually aligning the melting vessel 205 and casting mold 204 with proper contact angle and force, the apparatus can remember the set position and auto-align at injection. Then, the mover 208 moves up so that the melting vessel 205 is in the middle of the heater 206.

Vacuum the chamber 201 by the pump 202. Melt the alloying material powder in the melting vessel 205 by the heater 206. Then the mover 208 moves down to the set position where the quartz tube nozzle is exactly contacted with the mold gate as a manual operation. Open the valve 210 and the molten alloying material is pushed by the gas flow from the gas container 211

filled with the compressed gas through the gas conduit 209 and injected into the mold channel 203 of the casting mold 204.

The length of the mold channel 203 is 340mm, and the diameter thereof is 2mm. In this example, no demoulding agent is coated on the surface of the mold channel 203.

Repeat this example several times. The products obtained are all in the shape of rod and the length of these rods are all in the range of 150-200mm.

#### Example 2

The methods and conditions of this example are the same as those of example 1 except that the mold channel 203 is coated with a demoulding agent. In this example, the demoulding agent is a boron nitride emulsion which is obtained from the market.

Repeat this example several times. The products obtained are all in the shape of tube and the length of these tubes are all about 300mm.

#### Example 3

The methods and conditions of this example are the same as those of example 2 except that the demoulding agent is another boron nitride emulsion which is also obtained from the market.

Based on the observation, the property of forming a film of this demoulding agent is better than that used in example.

Repeat this example several times. The products obtained are all in the shape of tube and the length of these tubes are all about 340mm.

#### Example 4

The tube obtained from the example 2 is fixed by a tube clamp 301. A thin brass wire 302 is fed through the tube and is CNC-controlled to move inside the tube. Then remove the thick parts of the tube by the electrical sparking from the thin brass wire 302 at the tube. After this step, the tube with symmetrical wall thickness can be obtained.

Then immerge the tube in the electrolyte and connected to the electrode with DC power. The rough portion on the tube surface will be oxidized and dissolved in the electrolyte. Finally, a long, thin and homogenous bulk metallic glass tube is obtained.

The wall thickness of the obtained tube is 0.1mm, and the tolerance of the outer diameter and inner diameter is within  $\pm 0.01$ mm.

#### Example 5

The methods and conditions of this example are the same as those of example 4 except that the tube is obtained from the example 3.

The wall thickness of the obtained tube is 0.1mm, and the tolerance of the outer diameter and inner diameter is within  $\pm 0.01$ mm.

Although preferred embodiments of the present invention have been described for illustrative purposes, those skilled in the art will appreciate that various modifications, additions and substitutions are possible, without departing from the scope and spirit of the invention as disclosed in the accompanying claims.

## Claims

1. A method for fabricating a bulk metallic glass tube comprising the steps of:
  - a) melting an alloying material capable of yielding an amorphous alloy in a melting vessel;and
  - b) forcibly injecting the resultant molten alloying material into a through-hole mold channel, of which the surface is coated with a demoulding agent, of a forced cooling casting mold through the pressure difference between two ends of the molten alloying material, so that the molten alloying material in contact with the surface of the mold channel is then rapidly cooled down to below its melting point while the molten alloying material at the center of the mold channel still maintains a liquid state and flows forward continuously, leading to the formation of the tube.
2. The method for fabricating a bulk metallic glass tube of claim 1, wherein the demoulding agent is chosen from boron nitride emulsion and molybdenum disulfide emulsion.
3. The method for fabricating a bulk metallic glass tube of claim 1, wherein the molten alloying material is injected under a continuous pressure of a compressed gas.
4. The method for fabricating a bulk metallic glass tube of claim 1, wherein the steps of a) and/or b) are carried out in a vacuum or under an atmosphere of inert gas.
5. The method for fabricating a bulk metallic glass tube of any one of claims 1-4, wherein said method further includes the step of: c) utilizing low-speed wire electrical discharge machining to reshape the tube obtained by b).
6. The method for fabricating a bulk metallic glass tube of claim 5, wherein said method further includes the step of: d) electropolishing the tube obtained by step of c).
7. An apparatus for fabricating a bulk metallic glass tube including:
  - i) a melting vessel (205) for containing an alloying material capable of yielding an amorphous alloy;

ii) a heater (206) for heating and melting the alloying material contained in the melting vessel (205);

iii) a pressure difference generator for producing a pressure difference between two ends of the molten alloying material contained in the melting vessel (205);

iv) a forced cooling casting mold (204) provided with a through-hole mold channel (203) coated with a demoulding agent.

8. The apparatus for fabricating a bulk metallic glass tube of claim 7, wherein the demoulding agent is chosen from boron nitride emulsion and molybdenum disulfide emulsion.

9. The apparatus for fabricating a bulk metallic glass tube of claim 7, wherein the pressure difference generator includes a gas container (211) filled with a compressed gas, said gas container is connected to the melting vessel (205) through a gas conduit (209), and the open and close of the gas conduit is controlled by a valve (210).

10. The apparatus for fabricating a bulk metallic glass tube of any one of claims 7-9, wherein the apparatus further comprises a chamber (201) connected to a vacuum pump (202), the melting vessel (205), the heater (206) and the casting mold (204) are enclosed in the chamber (201).

11. The apparatus for fabricating a bulk metallic glass tube of any one of claims 7-9, wherein the apparatus further includes a clamp (207) and a mover (208), the melting vessel (205) is fixed by the clamp (207), the mover (208) is connected to the clamp (207) for adjusting the position of the melting vessel (205).

12. A bulk metallic glass tube fabricated by the method of any one of claims 1-6, wherein the length of the bulk metallic glass tube is longer than 300mm.

13. The bulk metallic glass tube of claim 12, wherein the wall thickness of the bulk metallic glass tube is from 0.1mm to 0.25mm.



14. The bulk metallic glass tube of claim 12 or 13, wherein the tolerance of the outer diameter and inner diameter of the bulk metallic glass tube is within  $\pm 0.01$ mm.

15. A coriolis flow meter equipped with at least one bulk metallic glass tube of any one of claims 12-14 as a sensing tube.

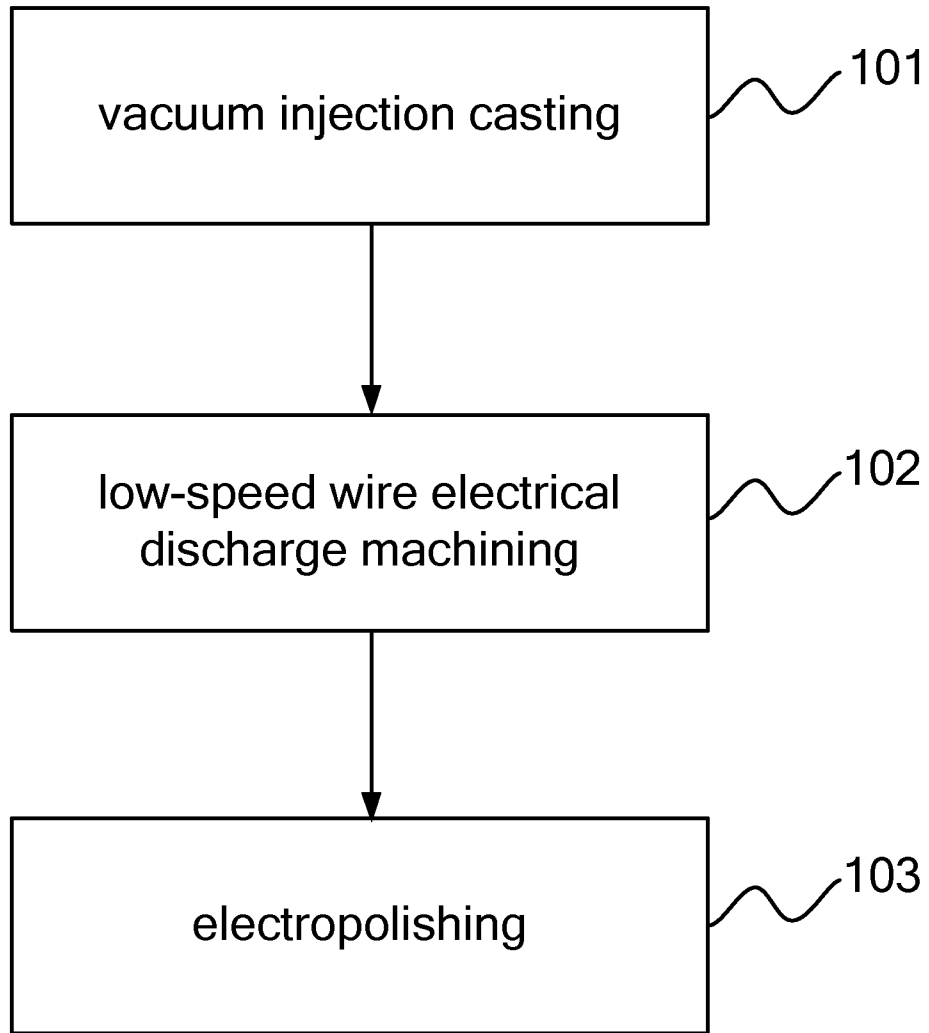


Fig.1

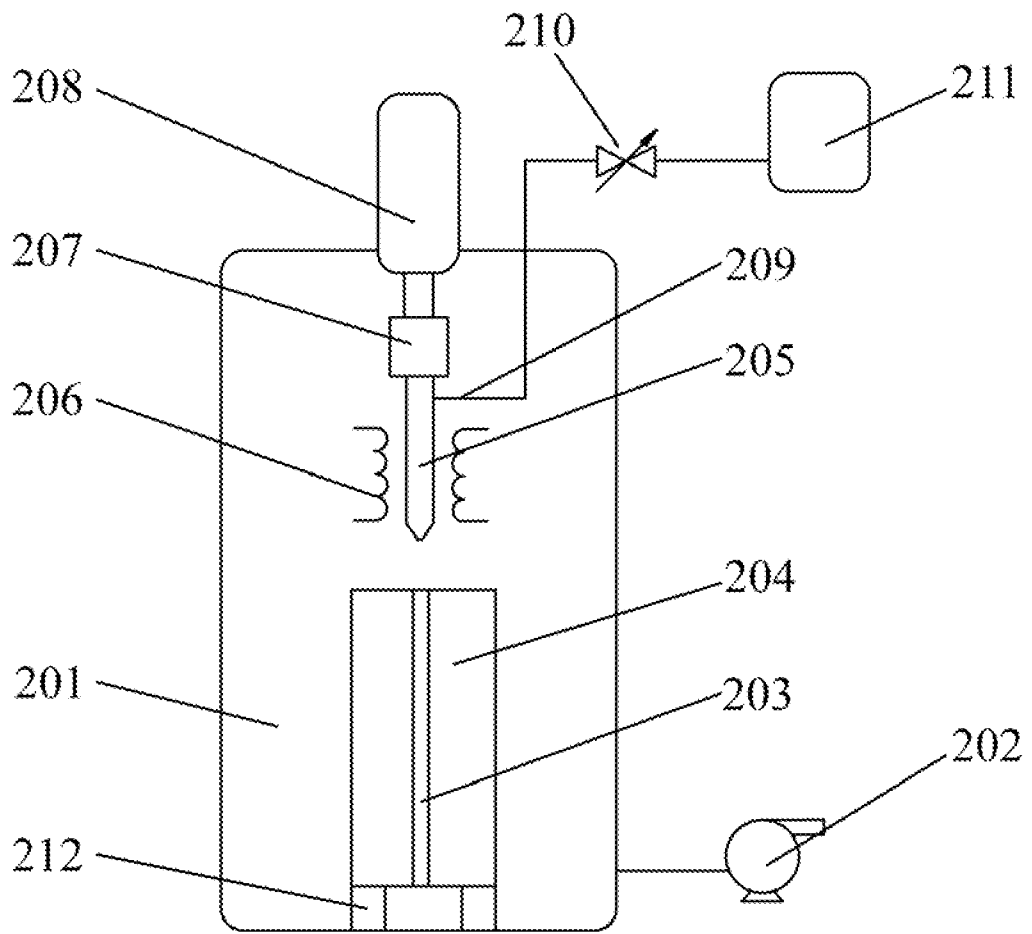


Fig.2

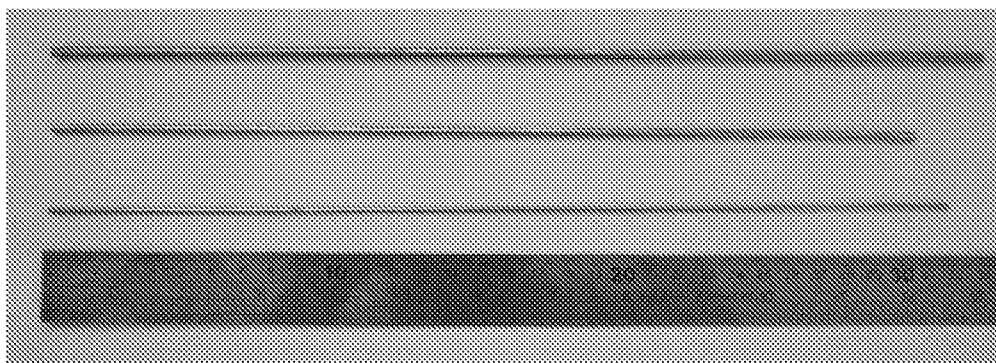


Fig. 3

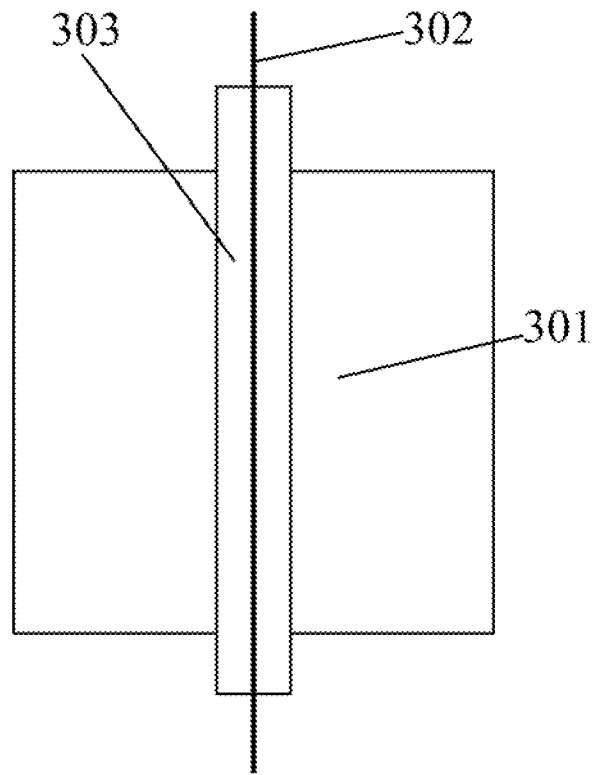


Fig. 4

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2011/078587

## A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet

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

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: B22D, B22C, C22C

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

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

WPI, EPODOC, CN-PAT, CNKI: amorphous, metal+ glass, glassy alloy, noncrystal+, non crystal+, tube?, tubular, pipe?, BN, boron, nitride?, MoS2, molybdenum, Mo, demo?ld+, release agent, molten, melt, melting, inject+, introduc+, film, coating?, disulfide?

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP2005279658A (INOUE A et al.) 13 Oct.2005 (13.10.2005) paragraphs [0007]-[0017], [0036], example 1	1-15
Y	YE, Fangmin, The Preparation and Characteristics of Fe <sub>36</sub> Co <sub>36</sub> Nb <sub>4</sub> Si <sub>4.8</sub> B <sub>19.2</sub> Tubes. Master Dissertation of Zhejiang Normal University. 2009. pages 20-21	1-15
A	JP5-253656A (DAIDO TOKUSHUKO KK et al.) 05 Oct.1993 (05.10.1993) the whole document	1-15
A	SU1662751A (UNIV KIEV SHEVCHENKO) 15 Jul.1991 (15.07.1991) the whole document	1-15
A	CN1939624A (MING Zhuwen et al.) 04 Apr.2007 (04.04.2007) the whole document	1-15

 Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:	“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
“A” document defining the general state of the art which is not considered to be of particular relevance	“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
“E” earlier application or patent but published on or after the international filing date	“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
“L” document which may throw doubts on priority claim (S) or which is cited to establish the publication date of another citation or other special reason (as specified)	“&” document member of the same patent family
“O” document referring to an oral disclosure, use, exhibition or other means	
“P” document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search  
10 Apr.2012 (10.04.2012)Date of mailing of the international search report  
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**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

International application No.  
PCT/CN2011/078587

Patent Documents referred in the Report	Publication Date	Patent Family	Publication Date
JP2005279658A	13.10.2005	JP4633377B2	23.02.2011
JP5-253656A	05.10.1993	NONE	
SU1662751A	15.07.1991	NONE	
CN1939624A	04.04.2007	NONE	

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2011/078587

Continuation of: second sheet, A. CLASSIFICATION OF SUBJECT MATTER

B22D 25/02 (2006.01)i

B22D 21/00 (2006.01)i

B22D 18/00 (2006.01)i

B22C 9/24 (2006.01)i

C22C 45/00 (2006.01)n