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The equipment for the preparation of micro and nanoscale metallic glassy fibers

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A supercooled liquid extraction method and apparatus for micro and nanoscale metallic glassy fiber preparation was developed. Using the fiber fabrication equipment, micro to nanoscale metallic glassy fibers with diameter ranging from 70 nm to 300 μm can be obtained by wire drawing in the supercooled liquid region of metallic glasses via superplastic deformation. The obtained metallic glassy fibers possess precisely designed and controlled sizes, high structural uniformity and high degree of surface smoothness. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4898018]

I. INTRODUCTION

Metallic glasses (MGs) with unique physical and mechanical properties provide model systems for studying some long-standing fundamental issues in liquids and glasses, and have potential structural and functional engineering applications.[1,2] Micro- and nano-scale fibers show attractive structural and functional properties and even unusual experimental phenomena.[3] Micro and nanoscale metallic glassy fibers (MGFs) could also possess desirable and unique mechanical and physical properties and glass-like thermoplastic process ability.[4,5] For example, the Co-based glassy microwires have giant magneto-impedance effect, which could be used as high-performance magnetic, stress and biological sensors,[6] and the drawback of brittleness of metallic glasses can be mitigated in the MGFs.[7]

The crystalline metallic fibers have a main drawback of controlling their dimensions and surface properties for various applications due to their poor formation ability using the existing fabrication methods.[8,9] Recently, several methods for fabrication of metallic glassy wires have been developed.[10–14] For example, the melt-extraction method without coolant was used to prepare continuous metallic glass wire,[11] however the grooves on the surface of wires cannot be avoided due to the contact between the wires and the wheel. An in-rotation-water spinning method has been successfully applied to fabricate the micro scale Fe- and Co-based MG wires,[10] but this method cannot continuously prepare MG wires, the chemical reaction between molten alloys and water is hard to be avoided, and the obtained wires are not uniform and have rough surface. For the Taylor method,[12] which is a continuous preparation method for metallic glass wire, the liquid temperature of the filling material must be higher than the softening temperature of the glassy wrappage, define wrappage and the reaction between the wrappage and the filling material usually happens at the drawing temperatures. On the other hand, the thermal expansion coefficient of the glass and the filling material must be close to each other and liquid filling material must be wet to the glass surface. Therefore, only very limited MGs wires can be prepared by this method,[13] and the wire surface is usually damaged by the vaporization of the filling material. Furthermore, the diameter of the metallic glass wire prepared by all the above methods is limited to the orders of 10–100 μm. Researchers have made intensive efforts to manufacture nanoscale metallic glass wires which should have remarkable unique mechanical and physical properties.[14–16] Metallic glass nanowires with a homogeneous amorphous structure have been reported, but the reproducibility and size are uncontrollable, and the wires cannot be continually prepared and the length is limited to micrometer scale.[14] Metallic glass nanowire can also be fabricated using nanoimprinting method,[17] the wires are highly nonuniform and are limited to nanometer scale. Poor structural uniformity and surface defects usually have harmful effects on the behavior and properties of the fibers formed using this method.

In this work, we designed and developed a combined machine to manufacture micro and nano scale MGFs by driving bulk metallic glass rods in their supercooled liquid state via superplastic deformation. The supercooled liquid extraction method is efficient for preparation of the MGFs with the virtues of low cost, continuous preparation, and high quality (they have very high degree of surface smoothness). The MGFs produced by the equipment can be precisely designed and controlled in size, structural uniformity, surface smoothness, and other properties depending on the composition and components.

II. DESIGN METHODOLOGY AND DESCRIPTION

To overcome the deficiencies of the prior methods for glassy fibers preparation, a supercooled liquid extraction method (SLEM) for micro and nano scale MGFs preparation was developed and the necessary apparatus was designed and produced. The basic principal of the SLEM method makes use of the wide supercooled liquid temperature region in which metallic glasses exhibit superplasticity. Micro and nano scale MGFs are fabricated from MG rods by forcing their viscous supercooled liquid (so-called supercooled liquid extraction method) similar to the natural preparation process of spider silk. The key for this method is to apply an appropriate drawing force when the glassy rod is heated to a viscous

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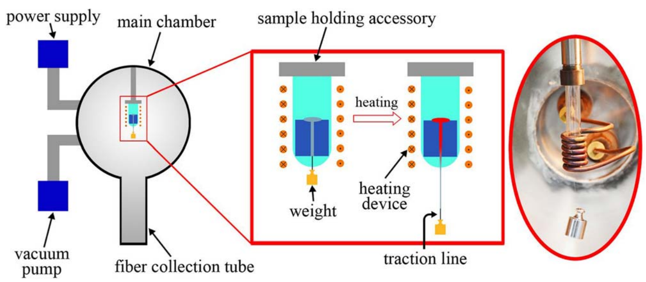

FIG. 1. General layout of metallic glassy fiber fabrication machine (left) and the schematic illustration for the principal of the supercooled liquid extraction method (right).

supercooled liquid state. In other words, the drawing forces should be applied when the viscosity of the supercooled liquid reaches a suitable value. The principal for the SLEM is schematically illustrated in the right part of Fig. 1. A weight is suspended by fixing it at the low end of the metallic glass rod through a metallic line, and the appropriate weight depending on the glassy system can be estimated (we will show that the appropriate pre-applied force for different metallic glasses can be estimated). Its photo is at the left part of Fig. 2. The weight is pre-applied. When the glassy rod is heated up to the supercooled liquid state to a suitable viscosity, the weight acting as the drawing force extracts the viscous liquid into a wire automatically and immediately. And the right of Fig. 2 shows the details of the SLEM assembly: A small low carbon steel cylinder is used for more rapid heat transfer from the heater to the MG rod. There is a hole in the steel cylinder and the diameter of the hole in the low carbon steel cylinder is larger than that of the glassy rods to avoid the contact between them. The MG rod is placed in the center of the hole, and then the rod together with the small cylinder is placed in a quartz glass tube. Finally all of them are placed in the middle of high-frequency induction heating coil. The assembly including sample and the heating device is fixed to the top of the stainless steel vacuum chamber. The assembly installed in the vacuum chamber works in a vacuum of 5×10^{-4} Pa. When the MG rod is rapidly heated up into its supercooled liquid state by the heat transferred from the low carbon steel cylinder, the pre-applied force provided by the weight automatically extracts the micro scale wire or MGFs from the supercooled liquid of the metallic glassy MG rod. The driving forces could also be applied by a rotating shaft linked with the low end of the glassy rod using a thin metallic wire for continuous MGFs preparation.[15] Nano scale MGFs are fabricated by the repeated driving of micro scale MGFs by SLEM.

The equipment for the SLEM includes several sections: a main chamber for installation of the assembly, an optional heating device, pump, a series of weights with different qualities, and a fiber collection tube as shown in the left part of Fig. 1. The mechanical and molecular pump system provides a high vacuum environment (less than 10^{-4} Pa). The working pressure of the argon atmosphere (with the purity of 99.999%) for the melting is 0.02 MPa. An optional heating device can be a high frequency induction heating coil or a resistance furnace. These two heating methods could be chosen according to the requirement of the experiments. Figure 3 shows the appearance of the equipment, and the photo of it is located in the upper left corner.

III. RESULTS AND DISCUSSIONS

A. The MGF forming ability

To manufacture the high quality of MGFs, the MG rod should have good glassy fiber forming ability. The forming ability of glassy fiber is determined by the glass-forming ability of the alloy. The large metallic glass forming ability, broad

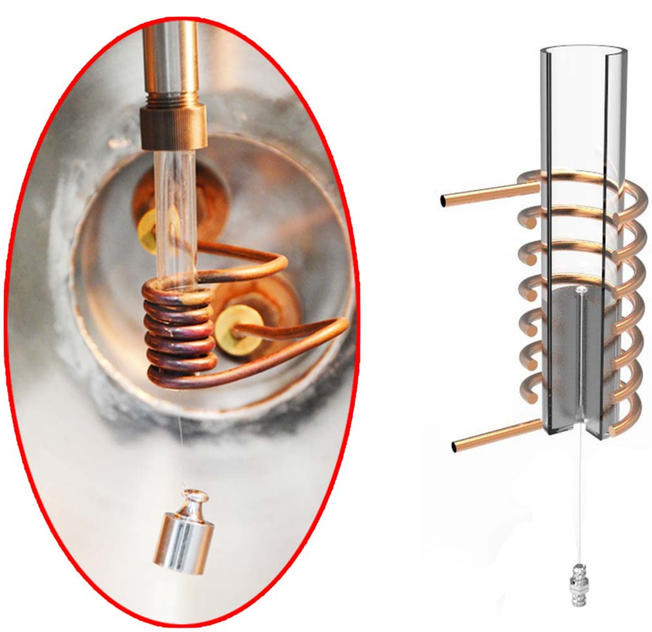

FIG. 2. The detail of the SLEM assembly (right) and its photo (left): A small low carbon steel cylinder, of which diameter and length is, respectively, 12.3 mm and 40 mm. There is a hole in the steel cylinder and the diameter of the hole in the low carbon steel cylinder is larger than that of the glassy rods. The MG rod is placed in the center of the hole, and then the rod together with the small cylinder is placed in a quartz glass tube.

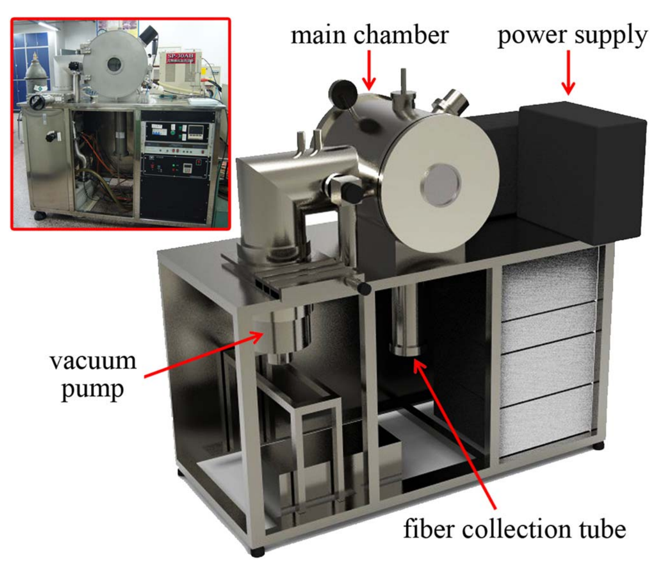

FIG. 3. The appearance of the equipment, and the photo of it is located in the upper left corner.

supercooled liquid region, and higher thermal stability are crucial factors for the MGF formation. The metallic glass-forming systems with larger glass-forming ability and broad supercooled liquid temperature region ($\Delta T_x = T_x$-T_g, where T_x is a crystallization temperature, and T_g is a glass-transition temperature) have the better MGF forming ability. In addition, the low viscosity η in the supercooled liquid region and the temperature dependence of η approaching T_g are key factors for producing MGF. A universal parameter f is proposed for evaluating the MGF forming ability:[18,19]

$$f \propto m \frac{\Delta T_x}{T_x}, \tag{1}$$

where m, the fragility is a measure of the temperature dependence of the viscosity around T_g. It is an index of how fast the viscosity increases while approaching the structural arrest at T_g. A liquid with larger m means that the liquid is to be shaped into an object in a short time, and small m means that it is to be shaped over a relatively long time. Actually, the fragility determines a glass-shaping machine's operation time and related to the MGF forming ability.

From Eq. (1), we can see that the MGF forming ability f can be readily determined by the thermodynamic parameters T_x, T_g, and m. From the value of f, we can estimate the relationship between the drawing force (the weight) and the diameter of the MGFs, and control the MGF size by selecting appropriate weight.[18,19]

B. The formation of the MGFs

The present SLEM and the equipment have successfully prepared a series of micro and nanoscale metallic glassy fibers with diameter arranging from 70 nm to 300 μm. Figure 4 exhibits the SEM imagine of the micro-scale and nano-scale $Pd_{40}Cu_{30}Ni_{10}P_{20}$ of MGFs.[18] Figure 5(a) is the x-ray diffraction spectrum of the $Pd_{40}Cu_{30}Ni_{10}P_{20}$ fiber. The typical broad diffuse peak similar to the amorphous alloy confirms that the fiber is full amorphous state. The differential scanning calorimetry study of the $Pd_{40}Cu_{30}Ni_{10}P_{20}$ fiber is shown in Fig. 5(b), which exhibits the fiber has a distinctive glass transition temperature, and the crystallization behavior further confirming the glassy structure.

It is extraordinary that the size of fibers can be controlled by adding or reducing the amount of the weights. The diameters of the MGFs range from 70 nm to 300 μm. The diameter decreases as the driving force decreases, and then it can be accurately controlled by choosing suitable driving force. The maximum diameter of the MG fiber can reach 100 μm, and minimum diameter can be as small as 70 nm. The reproducibility of the nano and microscale MGFs as high as 95% has been achieved by examining more than 70 different metallic glass rods.[18–21]

C. The properties of the MGFs

The obtained metallic glassy fibers are very uniform and continuous, and the surface of them is super smooth as shown in Fig. 4. One can see that even the nano-scaled MGF with diameter of about 200 nm has no voids, contaminants, and oxide layers in the enlarged surface of MGF as shown in Fig. 4. The surface smoothness of $Pd_{40}Cu_{30}Ni_{10}P_{20}$ fiber was examined by atomic force microscopy (AFM) and shown in Fig. 6. It can be seen that its surface smoothness has reached nanoscale. The attributes are due to the homogeneous structure and high corrosion resistance of metallic glass and steady viscous flow in supercooled liquid region as well as the advantages of this method.[18]

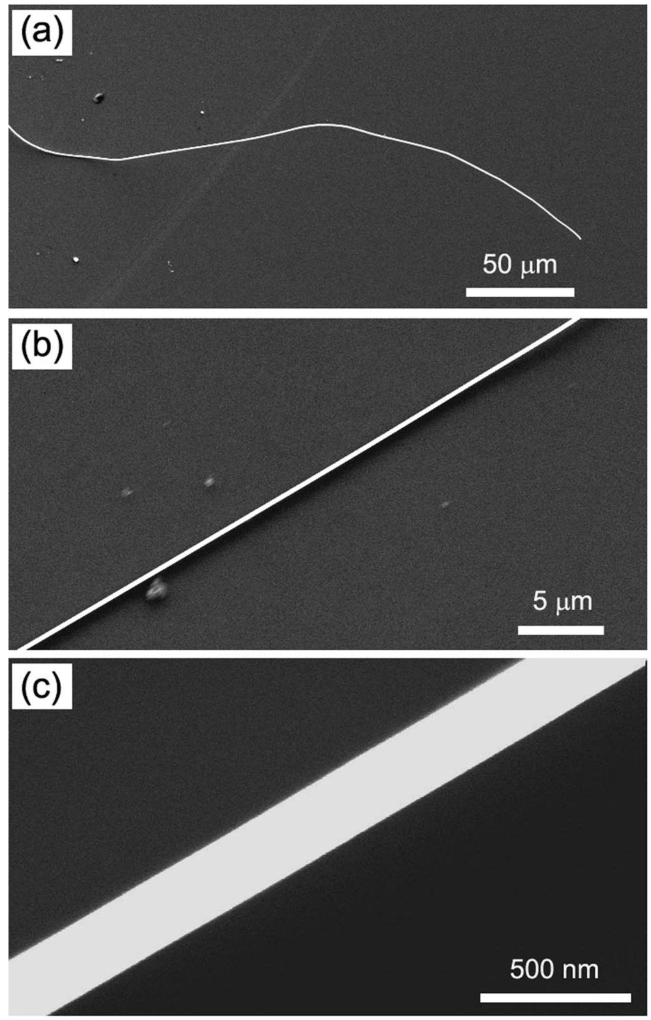

FIG. 4. SEM images of MGFs. (a) and (b) SEM picture of micro-scale $Pd_{40}Cu_{30}Ni_{10}P_{20}$ MGFs. (c) SEM picture of nano-scale $Pd_{40}Cu_{30}Ni_{10}P_{20}$ MGFs.

The MGFs possess unique mechanical properties. Figure 7 shows the tensile stress-strain curves for $Zr_{35}Ti_{30}Be_{27.5}Cu_{7.5}$ MGF (diameter ~16 μm) and $Pd_{40}Cu_{30}Ni_{10}P_{20}$ MGF (diameter ~16 μm) at a strain rate of 2×10^{-4} s^{-1}. The Young's modulus, tensile fracture strength, and strain limit for $Zr_{35}Ti_{30}Be_{27.5}Cu_{7.5}$ MGF are 94 GPa, 1.88 GPa, and 2.0%, respectively, and for $Pd_{40}Cu_{30}Ni_{10}P_{20}$ MGF are 74 GPa, 1.63 GPa, and 2.21%, respectively.[20] The MGFs can be severely bent as shown in Fig. 8. One can see that there are many shear bands around the bending area. Because of the high density shear bands, the MGF behaves high bending ability.

Electrical resistance strain gauges are useful strain sensing elements in many electromechanical transducers

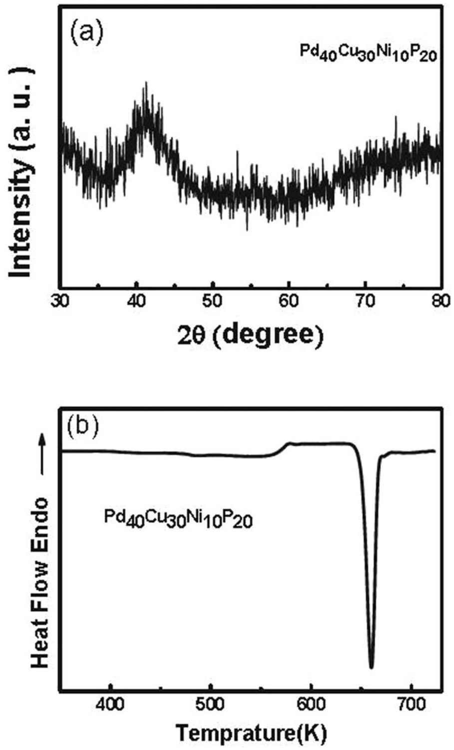

FIG. 5. (a) The x-ray diffraction spectrum from the $Pd_{40}Cu_{30}Ni_{10}P_{20}$ MGFs. (b) The DSC result which shows that the fiber has a distinctive glass transition temperature.

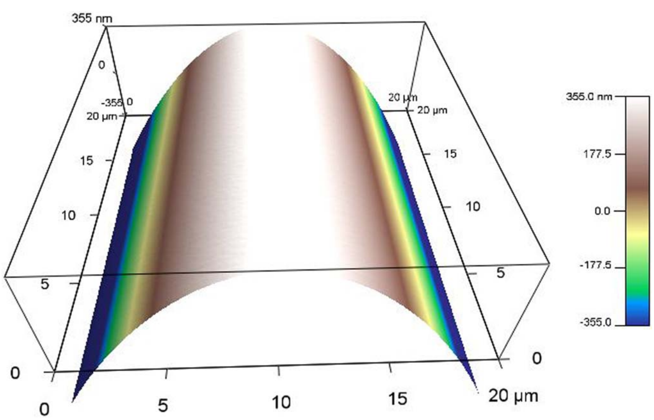

FIG. 6. The atomic force microscopy (AFM) picture of surface smoothness of $Pd_{40}Cu_{30}Ni_{10}P_{20}$ MGFs.

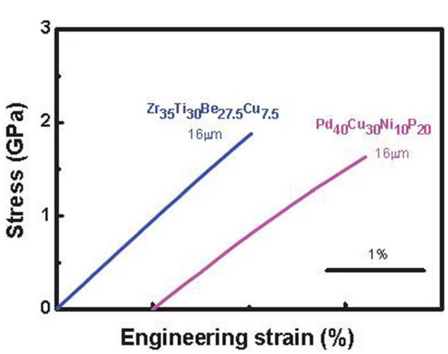

FIG. 7. The tensile stress-strain curves for $Zr_{35}Ti_{30}Be_{27.5}Cu_{7.5}$ MGFs and $Pd_{40}Cu_{30}Ni_{10}P_{20}$ MGFs at a strain rate of 2×10^{-4} s^{-1}SEM picture of bended $Pd_{40}Cu_{30}Ni_{10}P_{20}$ MGFs.

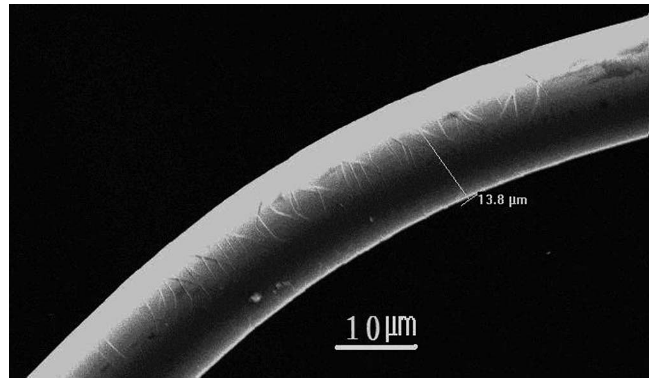

FIG. 8. SEM picture of bended $Pd_{40}Cu_{30}Ni_{10}P_{20}$ MGFs.

including load cells, pressure transducers, torque meters, accelerometers, force cells, displacement transducers, and so forth. It is found that the resistivity, gauge factor, elastic limit, and relative change in resistance of the MGF are superior to that of commercial crystalline electrical resistance strain gauges (ERSGs) piezoresistors. Combining with high flexibility, uniformity, smoothness, and nanoscale size in diameter, the MGFs are promising for piezoresistors of strain gauges especially for submicroscale ERSGs.[19] The smaller electrical resistance strain gauges are highly expected especially for micro-electro-mechanical systems, while the reduction of the size of strain gauge is restricted by the relatively low resistivity and poor processability of conventional piezoresistive alloys. A type of minuscule length scale strain gauges can be made by using a bare and single straight strand MGF with high resistivity, much smaller length scale, high elastic limits (2.16%) and especially the super piezoresistance effect.[20] Combining the nearly perfect linearity of the dependence of $\Delta R/R_0$ on ϵ, a relatively high gauge factor, high thermal stability and measurement reliability, high stiffness, and convenience for installation, the MGFSG is superior to that of the existing commercial SGs and close to ideal SGs. The MGF strain gauge is toward the ideal strain gauges and would have wide applications for electromechanical transducers and stress analysis.

IV. CONCLUSIONS

A combined machine, which can make micro and nanoscale metallic glassy fibers, was designed and built. The high quality metallic glassy fibers with diameter ranging from 70 nm to 300 μm can be fabricated. The metallic glassy fibers have precisely designed and controlled properties and size, high structural uniformity, and surface smoothness. The high quality MGFs with superior mechanical properties could stimulate a wide range of structural and functional applications of metallic glasses, and could have great application potentials.

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