Magnetic Fibers

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Abstract

The magnetic sensors based on soft magnetic effects of amorphous fibers are one of the highlights in scientific research in recent years. The amorphous fibers not only have excellent mechanical properties but also have unique magnetic properties, such as high permeability. As a result, sensors made of this kind of material can show the characteristics of sensitivity and durability. The processing and their advantages and disadvantages are mainly introduced in the chapter, and the properties reported in recent years are also summed up, including mechanical behavior, magnetic properties and shape-memory effects.

Keywords: magnetic sensor, amorphous fiber, serration behavior, glass-coated fibers, high entropy alloys

1. Introduction

In recent years, with the rapid development of information technology and automation technology, increasing requirements are put forward to the sensors, transducers and magnetic recording devices. Since the advent of amorphous fibers from 1970s, the research of these fibers has made a great progress. The amorphous fibers are defined as microfibers that have a diameter of dozens of micrometers and long-range disordered structure. This kind of fibers not only have high strength and some interesting mechanical properties [1], but they also exhibit unique magnetic effects such as large Barkhausen effect [2], Matteucci effect, giant magneto-impedance (GMI) effect [3] and giant stress-impedance effect, because of their unique internal stress distribution and magnetic domain structures [4]. As these characteristic magnetic effects are the foundation of various sensors, more and more attentions are attracted. In this chapter, four major preparation methods of amorphous fibers are focused,

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and the related work by the team of Y. Zhang in the University of Science and Technology Beijing (USTB) are summed up, including magnetic properties, mechanical behaviors and the shape-memory effect.

2. Preparation methods

The amorphous fibers prepared by different techniques are as follows: (1) in-rotating-water fibers, (2) glass-covered fibers and (3) melt-extracted fibers. Different preparation methods lead to different cooling rates, which in turn cause different properties. On the one hand, from outward appearance, the glass-covered fibers are different from the other two kinds of bare fibers, which can be used directly. Sometimes, the glass coatings need to be corroded for the performance tests and practical applications. On the other hand, these three kinds of fibers are different internally because of different processing techniques.

The conventional cold-drawing technique is a one-end drawing process at room temperature, where the prepared bar is drawn to pass a certain die hole. Although the surface quality can be improved through this simple process, the material selection is highly limited and the microstructure could probably be changed during this process. At present, this technology is used as a supplementary to the following three methods.

Amorphous fibers obtained by in-rotating-water quenching have been reported in 1980s. **Figure 1** shows the schematic diagram of this method. Melted by induction coil, alloys with specific composition are pressed by argon into the cooling water, which is rotating in the high-speed revolved copper mold. In this way, the fibers cool rapidly in the water, and therefore, continuous and perfect fibers are gained, which are usually smooth and have circular

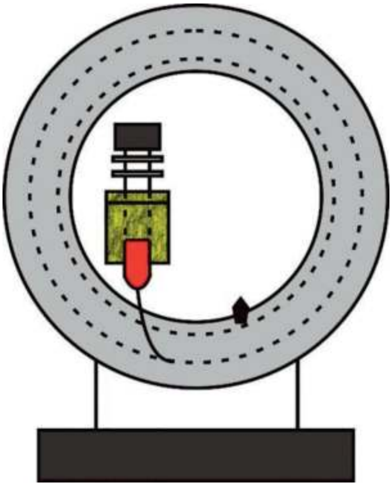

Figure 1. The schematic diagram of in-rotating-water quenching technique.

cross sections. However, the technique of producing amorphous fibers by in-rotating-water quenching is restricted greatly by the composition. This method can only be used in Fe-based, Co-based and CoFe-based alloys till now [5, 6]. The fibers also easily react with oxygen in the cooling water and thus degrade the performance. Moreover, because of the experimental conditions and the cooling rate, the diameters of these fibers are about 100 μm and thus decrease the degree of amorphization. Sometimes, these fibers should be cold drawn to decrease the diameter. Because this method is relatively simple, it develops rapidly at home and abroad and is used to produce continuous fibers at the earliest. For example, many universities developed several kinds of in-rotating-water fibers and studied their properties and technological parameters from 1990s.

A process for the production of fine metal fibers directly from the melt was first reported by Taylor in 1924 [7], and then it was improved by Ulitovsky and Wagner. As a result, this glass-coated melt spinning method is also called as Taylor-Ulitovsky method. **Figure 2** shows the schematic diagram of this method. The closed-end Pyrex glass tube and the master alloy placed in it are heated by an induction coil to the melting point. The softened glass and the liquid alloy in it are drawn out by the external force and then they are cooled down quickly by water for the purpose of quenching. Fibers with relatively small diameters are obtained through this process, and they twine around a rotating cylinder by the winding system for further use. The scanning electron microscopic (SEM) image of a glass-coated amorphous fiber is shown in **Figure 3**. The fibers are winded on a receiving coil, whose rotating speed is determinant for the fibers' diameter and the glass thickness, and hence, the fibers' properties. The diameter of the fibers ranging from 0.08 to 80 μm can be obtained. This basic method offers a route for the manufacture of metallic fibers in a single operation directly from the melt. Due to the high critical quenching rate [10^4 K/s (Kelvin temperature per second)], metastable, amorphous or supersaturated state phases can be obtained. Moreover, the coated glass

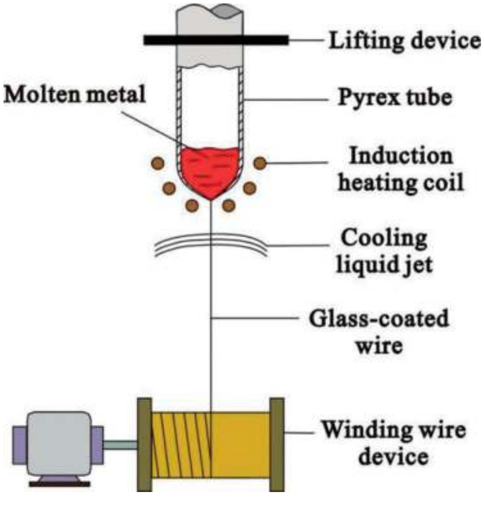

Figure 2. The schematic diagram of glass-coated melt spinning technique [12].

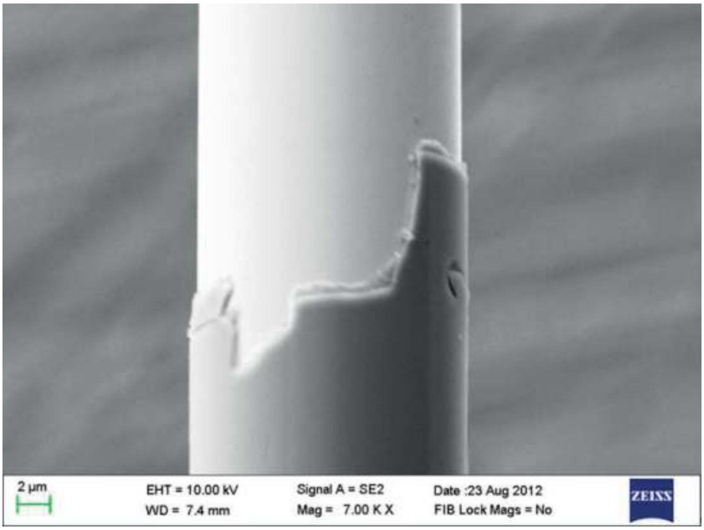

Figure 3. The SEM image of a glass-coated amorphous fiber [12].

acts as a shielding layer to improve the corrosion resistance. All these advantages contribute to promising applications such as micro electromechanical system [8]. However, the drawbacks are the limited alloy system, because this preparation method depends on the melting point of metals and the wetting between molten metal and glass. At present, this technology is relatively mature and the related research is broad in many universities [9]. Various kinds of glass-coated fibers have been obtained by the equipment (**Figure 4**) developed by our group. Our team reported Cu-15.0 at.% Sn microwires with diameters of about 184 μm [10] and $Co_{69.5}Fe_{4.35}Cr_1Si_8B_{17}$ [11] microwires with diameters of about 30 μm, which show smooth and almost flawless surface, implying that the glass-coated melt spinning method is a very effective technique in producing the high-quality microwires. In addition, Li et al. [12] prepared high-quality glass-coated $Fe_{76.5-x}Cu_1Nb_xSi_{13.5}B_9$ ($x = 0, 1, 2, 3, 3.5$) fibers that are also obtained by our equipment.

Put forward by Maringer at about 1974 at the earliest, the melt-extraction technique attracted much attention and was used to prepare metallic amorphous fibers at 1990s [13]. This technology is an advanced shaping methods for low dimensional materials. As shown in **Figure 5**, the working principle of this technique is as follows. Under high vacuum, the top of the alloy sample is melted by the induction heater and then extracted by the sharp edge of the rotating copper wheel. Under the combined effect of viscosity, surface tension and gravity, amorphous fibers are produced, and the cooling rate is as high as 10^6 K/s. The bare fibers with small diameters (about scores of micrometers) and a great degree of amorphization are obtained. In practice, the melt-extraction technique can be used to prepare strips, plates and fibers with different materials, the scope of which is extremely wide. This means that the unique technology overcomes the shortcomings of the three methods above. Furthermore, it has been proved that the products possess excellent electrical, magnetic and mechanical properties, as well as

Figure 4. The picture of the glass-coated fibers drawing equipment [12].

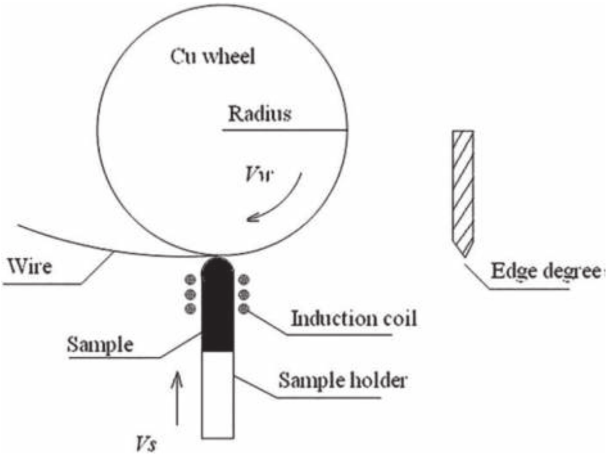

Figure 5. The schematic diagram of melt-extraction technique [14].

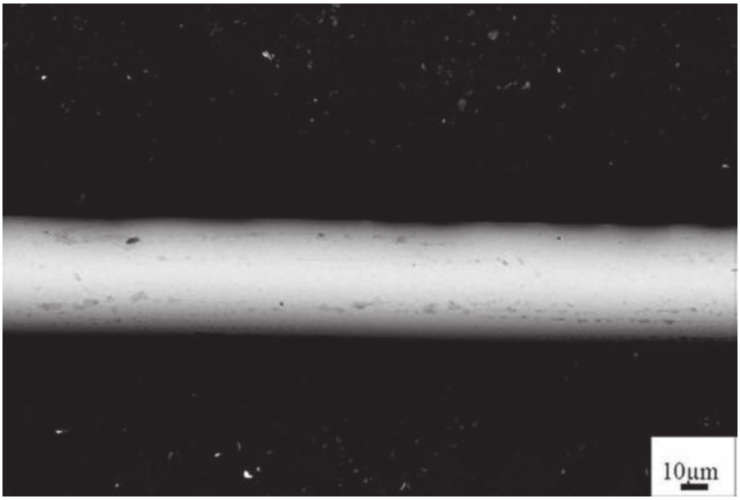

Figure 6. The SEM image of a melt-extracted fiber [14].

has high geometric symmetry. The difficulties lie in the complex preparation process. The influence factors of this process cannot be controlled exactly, and the quantitative relationship between technological parameters and the qualities is not very clear till now. At present, many universities in China are carrying out the related researches about the melt-extraction technique, and many high-performance metallic fibers have been prepared. Melt-extracted $Zr_{50.5}Cu_{27.45}Ni_{13.05}Al_9$ [14], $Co_{69.5}Fe_{4.5}Cr_1Si_8B_{17}$ [15] and Cu-Zr-Al [16] amorphous wires with almost flawless surface and precise circularity were produced by Liao (**Figure 6**), implying that the melt-extraction method was very effective in producing the high-quality wires.

3. Properties

3.1. Mechanical behavior

It is well known that the bulk metallic glasses exhibit better mechanical properties than the traditional alloys. For example, the compressive strength of CoFeTaB bulk amorphous alloys reaches up to 5185 MPa, which creates a new record of strength in metallic alloys. The amorphous fibers inherit this fine mechanical performance besides the good physical and chemical properties. In addition to the electrical and magnetic properties, the mechanical properties should be taken into special consideration to ensure a stable and reliable work. A great deal of theoretical and experimental works has indicated that the loading mode [17] and the sample size used for testing can affect the mechanical properties of amorphous alloys remarkably [18, 19]. Most of the reported metallic glass systems show considerable plasticity in compression test [20], while their tensile properties are relatively poor. Because of the normal tension stress effect [21], their tensile plasticity is poor and catastrophic fracture will happen during tensile test, which is the major limitation of the use of bulk metallic glass. Nevertheless, recent researches have shown that when the tested sample size is reduced to the nanometer scale [22, 23], the mechanical properties will become obviously different. A large plastic strain can be obtained because the shear bands no longer occur during both tension and compression. As a result, the metallic glasses with small sample sizes exhibit different deformation behaviors compared with the bulk-sized ones, which also suggests that the mechanical properties of amorphous fibers are slightly different from that of bulk amorphous alloys.

During recent years' research, the team of Y. Zhang has reported many kinds of amorphous fibers with good mechanical properties. Most of the fibers display only an elastic deformation behavior and catastrophic fracture without yielding because of their amorphous nature. Zhao et al. [24] prepared $[(Zr_{43}Cu_{50}Al_{7})_{99.5}Si_{0.5}]_{99.9}Y_{0.1}$ (Zr43) and $Zr_{50.5}Cu_{27.45}Ni_{13.05}Al_{9}$ (Zr50.5) fibers, and they all show high tensile fracture strength of 1600 MPa and a large elastic limit reaching approximately 2%. The tensile strength value increases with the increase in the content of Al. Liao et al. [14] reported $Zr_{50.5}Cu_{27.45}Ni_{13.05}Al_{9}$ alloys with fracture strength reaching 1800 MPa and elastic limit reaching 2%, and the Weibull modulus is as high as 81. The glass-coated $Fe_{76.5-x}Cu_{1}Nb_{x}Si_{13.5}B_{9}$ ($x = 0, 1, 2, 3, 3.5$) amorphous fibers show such a high strength as 2500 MPa, with the Weibull modulus reaching above 20, saying that the high strength is reliability [12].

It is also found by Liao that the $Co_{69.5}Fe_{4.5}Cr_{1}Si_{8}B_{17}$ [15] and Cu-Zr-Al [16] metallic glassy wires exhibit unusual nonlinear deformation behavior with irreversible elongation (**Figure 7**), and the analysis indicates that this nonlinear deformation is related to the formation of subnanometer voids coalesced from flow defects under tensile stress. The work suggests that the tensile failure of the glassy fibers is controlled by both the normal stress and shear stress. The dominant stress is the shear stress, and the normal stress lowers the energy barrier for the atoms to flow. The shear bands form initially on the tensile surface and then propagate toward the neutral layer.

3.2. Magnetic property

Excellent physical properties such as soft magnetic properties and unique expansibility can be obtained in amorphous materials. It has been indicated that the saturation magnetization of Fe-based amorphous alloys is more than 1.5 T, coupling with a low coercive force of about 1 A/m^2. Li reported a kind of glass-coated $Fe_{76.5-x}Cu_{1}Nb_{x}Si_{13.5}B_{9}$ ($x = 0, 1, 2, 3, 3.5$) fibers [12]. The results show that the magnetic behavior is greatly influenced by the structure and composition of the fibers, and it also suggests that the coercivity of the amorphous structures is far lower than that of the coarse crystal ones. Compared with all the other kinds of fibers, the glass-coated amorphous FeCuNbSiB fibers have the best comprehensive performance, which have both relatively great magnetic properties and tensile properties.

The giant magneto-impedance (GMI) effect, which is the foundation of magnetic sensors, has been found in amorphous materials in recent years. Magnetic sensors can be broadly applied in the field of geology, measuring, traffic and military, and some important parameters of the sensors include the sensitivity, stability, volume, and power consumption. The

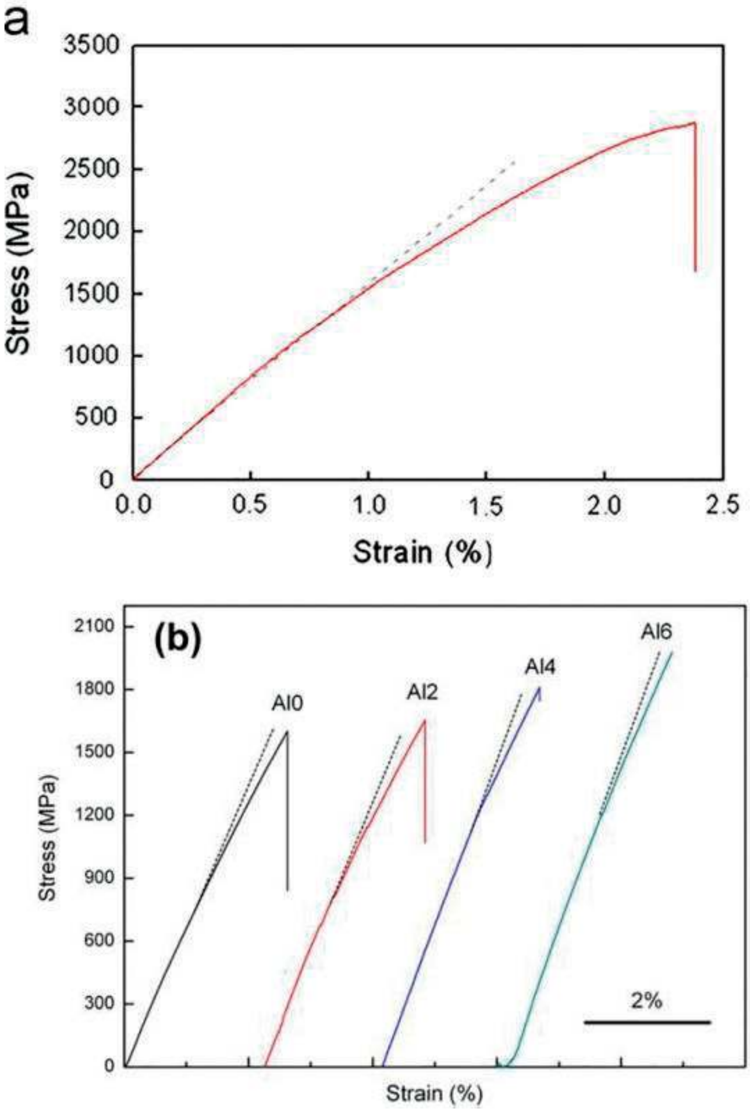

Figure 7. The unusual nonlinear deformation behavior of (a) $Co_{69.5}Fe_{4.5}Cr_1Si_8B_{17}$ [15] and (b) Cu-Zr-Al [16] metallic glassy fibers.

traditional magnetic sensors include Hall effect sensors, giant-magnetic-resistance (GMR) sensors and fluxgate sensors; while in 1994, the GMI effect was found in amorphous fibers by Professor Mohri and Panina [3], which significantly enhanced the performance of magnetic sensors. Soon afterward, the same effect was also found in other shapes, for instance, ribbon and film. But in practice, compared with ribbon samples, fibers show bigger GMI effect and sensitivity at room temperature with their highly axisymmetric structure, which meet the requirements of a number of new micromagnetic sensors.

Under the applied magnetic field, when the alternating current is flowing into the amorphous-sensitive element, there is an impedance change in it. If the voltage across the sensitive element is measured, the changes of voltage with the change of applied magnetic field can be seen. As a result, the giant magneto-impedance effect is referred to as the impedance changes along with the change of magnetic field. The GMI ratio can be expressed as:

$$\mathrm{GMI} = \frac{\Delta Z}{Z} = \frac{Z(H) - Z(H_{\max})}{Z(H_{\max})} \times 100\,\%, \tag{1}$$

where Z is the impedance, ΔZ is the change of impedance, H is a certain magnetic field strength and $H_{\max}$ is the maximum value of the applied magnetic field.

The GMI effect of amorphous fibers can be attributed to the strong skin effect and the special magnetic domain structures, which are related to the stress state [4]. The internal stress usually appears during solidification and preparation, and the different thermal expansion coefficient between glass and fiber can also lead to unique internal stress states, which in turn contribute to the special domain structures. In amorphous fibers with negative magnetostrictive coefficient, the magnetic domain is axial in the outer shell and circumferential in the inner core, while the domain, which is in the inner core, will change into radial after the glass coat is applied, because of the increased axial stress, as is shown in **Figure 8**.

As indicated above, due to the circular magnetic anisotropy caused by the inner stress and magnetostrictive effect, the annular magnetic domain is formed on the surface. The passed electric current creates an easy axis, which lead to the movement of domain wall and the annular magnetization, while the applied longitudinal magnetic field prevents the change of the annular magnetic flux. As a result, the transverse magnetic permeability varies sensitively with changes in the external magnetic field. Then, the varying transverse magnetic permeability acts

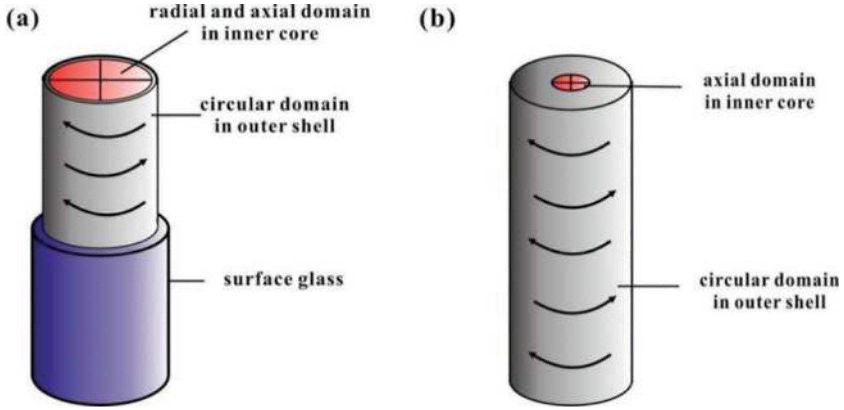

Figure 8. Magnetic domain distribution of (a) as-cast and (b) glass-removed fibers [12].

as a promotion to the changes in the impedance. This is because the impedance is a function of skin depth, whose mathematical expression is

$$\delta_m = \sqrt{2\varrho/\mu\omega}\,, \tag{2}$$

where ϱ is the electrical resistivity, μ is the transverse magnetic permeability and ω is the angular frequency of the alternating current. Finally, the changed rules of external magnetic field are obtained from the changes of impedance.

In the aspect of material, the magnetostrictive coefficient of Co-base amorphous fibers is -10^{-7}, approximately thought of as zero, and this kind of fibers has high corrosion resistance, tensile strength and domain wall energy density, plus special magnetic domain structures, and thus, Co-base amorphous material is a kind of representative GMI materials [25]. The sensitivity of the giant magneto-impedance effect is affected by various factors, such as material types, the number and diameter of fibers and the glass coat. García et al. [26] discovered that in $Co_{59.2}Fe_{4.8}Ni_{11}B_{14}Si_{11}$ amorphous fibers, the GMI ratio increases first and then decreases with the increase in fibers under high-frequency current of about 500 MHz, whereas the value of ratio decreases gradually under low-frequency current. Zhang et al. [27] studied the influence of diameter on GMI ratio. The results show that the GMI ratio first increases and then decreases with the increase in diameter, and the coated glass also has effect on the GMI ratio. Zhao et al. [11] suggests that the cold drawing has a great influence on the GMI effect. A transition from single-peak (SP) to double-peak (DP) GMI behavior is observed in $Co_{69.5}Fe_{4.35}Cr_1Si_8B_{17}$ microwires after cold drawing, which is caused by the induced circumferential stress. This circumferential stress appears during cold drawing, and it results in the significant changes of the surface magnetic anisotropy, which changes from helical domains to circular domains. The GMI ratio as well as field sensitivity is improved significantly after cold drawing and that would be significant for application.

3.3. Shape-memory effect

In addition, a significant shape-memory effect and superelasticity were found in Y. Zhang's research group. They prepared the Cu-15.0 at.% Sn microwires by glass-coated melt spinning and reported that the bent sample, which were deformed to "U" shape in liquid nitrogen, remembered its initial shape and recovered by itself at room temperature. Standing in sharp contrast to the slightly shape-memory effect in single crystal of Cu-15.0 at.% Sn alloys, this phenomenon can be explained by the high cooling rates suppressing the precipitation of other phases, and thus very good shape-memory effects are obtained. Furthermore, the plasticity of these kinds of fibers is great and the fracture strain reaches 14.2%, while it is usually brittle when the fibers are in the polycrystalline state. From a long-term development, the experiments and results will contribute to solving the limitation of Cu-based shape-memory alloys, which will also enlarge the application range of the Cu-based alloys and promote the development of shape-memory alloys.

4. Conclusion

The main preparation methods, as well as their advantages and disadvantages, are mainly introduced in this paper, and the properties reported in recent years are also summed up, including good mechanical properties, magnetic properties and shape-memory effects. It now appears that the preparation technology of amorphous fibers is relatively mature, and we can choose the most appropriate method according to the basic characteristics of the alloy system and our requirement. In terms of the properties and applications, the soft magnetic properties and special magnetic effects of the fibers have been fully studied and successfully applied to the magnetic sensors, achieving the goals of miniaturization. However, other performance such as shape-memory effect has not been applied in practice, so lots of work in this aspect need to be carried out.

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