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Rejuvenation in Hot-Drawn Micrometer Metallic Glassy Wires *

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We report an enhanced rejuvenation in hot-drawn micrometer metallic glassy wires (MG wires) with the size reduction. Compared to metallic glasses (MGs) in bulk form, the modulus and hardness for the micro-scale MG wires, tested by nanoindentation methods, are much lower and decrease with the decreasing size, with a maximum decrease of ∼*26% in modulus and* ∼*17% in hardness. This pronounced rejuvenation is evidenced by the larger sub-*$T_{\rm g}$ *relaxation enthalpy of the MG wires. The pronounced rejuvenation is physically related to the higher energy state induced by a combined effect of severely thermomechanical shearing and freezing the shear flow into a constrained small-volume region. Our results reveal that the internal states and properties of MGs can be dramatically changed by a proper modulation of temperature, flow stress and size.*

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Metallic glasses (MGs), as a metastable material rapidly quenched from the liquid, have numerous microstructural configurations and energy states that correspond to their various properties and strongly depend on their formation procedure.[1,2] Intriguingly, the aged or as-quenched MGs can be rejuvenated with the injection of external energy. Rejuvenation, the inverse of physical ageing, allows for the configurational excitation across a complex potential energy landscape and benefits to improve the plasticity of MGs. Many studies revealed that the applied stress or temperature change could lead to the rejuvenation of MGs, which is characterized by a softening on the hardness or the modulus, and an improvement of the plasticity.[3−5] Intrinsically, the change of these properties has been related to the structural disordering or enhanced degree of structural heterogeneities in MGs.[6,7]

As a basic parameter of solid materials, elastic moduli are sensitive to the internal structure configuration of materials and play an important role in understanding their properties.[8] This is particularly appropriate for glasses because their amorphous atomic structure is too difficult to be characterized with conventional experimental methods.[9,10] For MGs, the elastic moduli are found to closely correlate with other physical properties, such as glass transition, relaxations and deformations.[11−13] The elastic properties related to their internal structure of MGs can be tuned with rejuvenation. However, the reported change in elastic properties of MGs during the rejuvenation is generally small, i.e., MGs can be rejuvenated to a higher energy state with a more heterogeneous structure by cryogenic thermal cycling treatments, yet only with a few percent of decrease in modulus.[6] On rejuvenation of MGs, thermomechanical treatments have been proved to be an effective way regardless of the aging during heating,[14−18] which implies the importance of the stress induced rearrangement of atomic structure on rejuvenation. For glasses, thermoplastic processing is also the basis for the thermal molding methods in various engineering applications. In addition, it has been found that when the shear flow is constrained around a local region such as a shear band, the MG could achieve a state of extreme rejuvenation with a significant softening as large as 40% on the hardness, indicating a combination effect of flow stress and size.[4] Therefore, it is interesting to examine the rejuvenation of MGs under a proper combination of temperature, flow stress and size.

In this Letter, we study the change of mechanical properties of hot-drawn MG wires using the nanoindentation method. With size reduction, we find a pronounced softening on both Young's modulus and hardness for MG wires. The softening of MG wires shows a clear size dependence, with a maximum decrease of

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∼26% on Young's modulus and ∼17% on the hardness, as compared to those of bulk MGs. The softening is physically related to the higher energy or rejuvenated state induced by a combined effect of severely thermo-mechanical shearing and freezing the shear flow into a constrained small-volume region.

Considering the excellent glass forming ability and thermoplastic ability, we choose $Pd_{40}Cu_{30}Ni_{10}P_{20}$ (at atomic percent) MG to conduct this study. Alloy ingots were prepared by arc melting appropriate amounts of high purity elements in a Ti-gettered argon atmosphere. MG rods with different diameters (1 mm and 4 mm) were made by copper-suction casting method. MG wires with diameters ranging from ∼60 µm to ∼200 µm were made by hot-drawing the 1-mm-diameter MG rods in super-cooled liquid region.[19] The amorphous nature of all specimens was verified by the x-ray diffraction (XRD). Nanoindentation tests were performed on a commercial Agilent Nano-Indenter G200 system with continuous stiffness measurement (CSM) core. A Berkovich indenter was used to indent into a depth of 400 nm at a quasi-static strain rate on the mirror-polished cross sections of the MG samples. Young's modulus and hardness of the MG samples were obtained by the Oliver–Pharr method.[20] Due to the small cross section for the micrometer wires, we perform the nanoindentation tests on at least three samples for each diameter. The values of Young's modulus and hardness for each size of MGs were averaged over these samples. The relaxation spectrum was obtained by a commercial differential scanning calorimetry (DSC) system (PerkinElmer 8000), with a heating rate of 20 K/min.

The MG wires were made by drawing MG rods in supercooled liquid region as shown in Fig. 1(a). The observation to the hot-drawn MG wires by a scanning electron microscope (SEM) is shown in Fig. 1(b). One can see that the hot-drawn MG wires have excellent diameter uniformity and surface quality, even the original as-cast MG rod has some surface defects such as fins, scraps and bulges, suggesting significant plastic flow behavior during their formation. Figure 2(a) shows the typical load-depth curves from the indentation tests for the MG samples with different diameters, and the inset, as an example, shows an indentation on the polished cross sections of an MG wire. As is seen, on loading to the same depth of 400 nm, the required force for the MG wires is much smaller than that of the bulk MG rod and decreases with the gradually decreasing diameters. The maximum reduction for the loading force reaches ∼25%. Compared with the MG rod, these MG wires exhibit a softer mechanical property. On unloading, the indentation force on the MG wires decreases slower than that on the MG rod, with a larger elastic recovery after removing load. This indicates that the elastic properties of MG wires are much softer, yet their elastic limit is much larger than that of bulk MG rods. Also, elastic properties of MG wires show a clear size dependence.

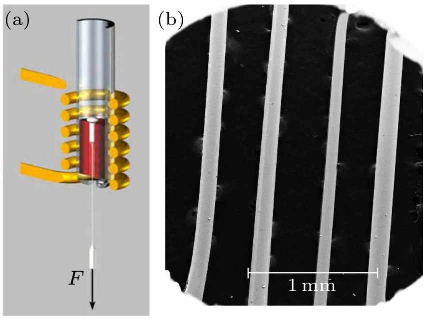

Fig. 1. (a) The schematic diagram for the fabrication process of an MG rod being drawn into an MG wire in supercooled liquid region. (b) The SEM image of the hot-drawn MG wires showing good diameter uniformity and surface quality.

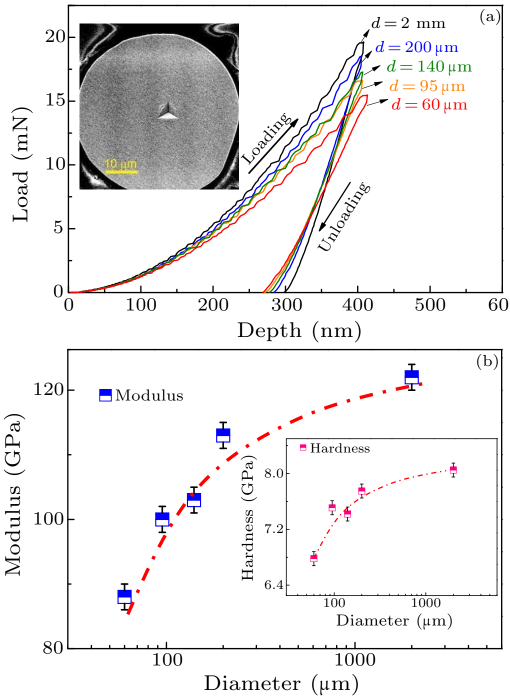

Fig. 2. (a) The load-depth curves obtained by nanoindentation tests for the MGs with different diameters. Inset: a typical indentation on the cross section of an MG wire. (b) The variation of measured modulus and hardness (inset) with sample diameter, showing a clear size dependence with a maximum reduction of ∼26% in modulus and ∼17% in hardness.

A more direct and quantitative insight into softening of MG wires is reflected by the measured modulus and hardness (inset) for the MG samples with different diameters, as shown in Fig. 2(b). The modulus of the MG samples with different diameters is evaluated from the unloading curve using the Oliver–Pharr method. Both the modulus and hardness of MG wires are lower than that of the bulk MG rod, and decrease with size reduction. As diameter decreases from 2 mm to 60 µm, the reduction in modulus and hardness, respectively, can be as high as ∼26% and ∼17%.

The properties of MGs are closely related to their internal energy states. In general, the internal energy state of MGs is characterized by the stored energy exceeding the balance state, which can be manifested as an exothermic peak below glass transition temperature T_g in its DSC trace. Figure 3 shows the comparison of the thermal relaxation spectra between the 60-μm-diameter MG wire and the 2-mm-diameter MG rod. It is clear that the exothermic peaks of the wire are more pronounced, especially on the first peak. The total released sub-T_g relaxation enthalpy ΔH_{rel} is calculated by integrating the area under exothermic peaks, e.g., the shaded area for the bulk sample. The calculated relaxation enthalpy ΔH_{rel} of the wire is ~28% higher than that of the bulk rod. This suggests that the MG wires are at an internal state of higher energy, with a higher free volume content, which is a signature of rejuvenation in MGs. On atomic structure, the configuration state with higher stored energy is more disordered and contains more soft spots or flow units,[6] which have a lower modulus, looser atomic packing, higher atomic mobility, and are particularly effective in initiating flow and improving plasticity of MGs.[21–25]

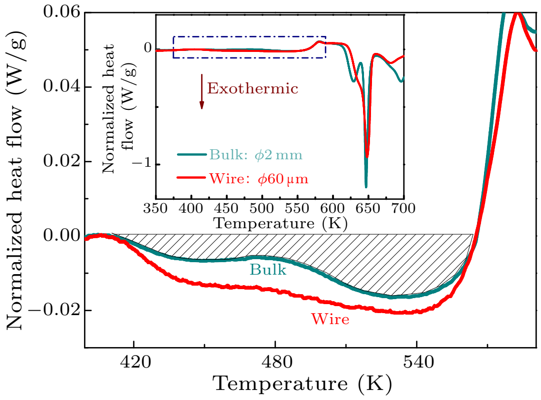

Fig. 3. The comparison of the relaxation spectrum in DSC traces between the bulk MG rod with a diameter of 2 mm and the MG wire with a diameter of 60 μm. Compared with the bulk MG rod, the sub-T_g exothermic peaks of the MG wire are much larger with an increase of ~28% in relaxation enthalpy ΔH_{rel}.

The rejuvenation of MGs is usually achieved by thermomechanical processing such as the creep at high temperatures or the cryogenic cycling. The rejuvenation induced by these methods is often accompanied by a significant decrease in yield strength or hardness, yet a small decrease in the elastic modulus. The reason lies in that the rejuvenation of MGs by those methods is related to the nanoscale structural heterogeneities, which may have non-affine thermal strain due to the mismatch between the nanoscale heterogeneities (such as the “hard" regions and the “soft" regions) when they responded to external stress or temperature field. As a result, an enhanced structural heterogeneity at nanoscales can be found in the rejuvenated MGs. Since the plastic flow is often initiated in the nanoscale soft regions, the rejuvenation is much more related to the decrease of yield strength or hardness. In contrast, the elastic modulus is physically related to the interatomic distance in the amorphous structure, therefore the variation of elastic modulus is usually small during the rejuvenation. However, in our current studies, it is found that the decrease of Young’s modulus of MGs is as large as 26%, which is even larger than their variations in hardness (~17%), indicating that the hot-drawing or thermoplastic deformation may have a totally different effect on the amorphous structure as compared to previous thermomechanical methods.

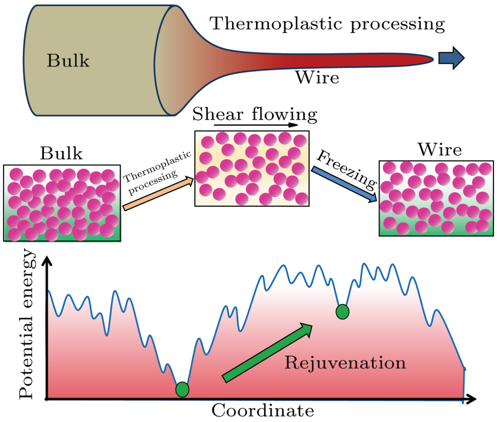

Fig. 4. The schematic illustration for the underlying physical origin of the softening in the hot-drawn MG wires. The atomic structure of MG rods undergoing thermoplastic deformation is severely rearranged through the cooperative motions of STZs, which are frozen in the MG wires under a high cooling rate, leading to the rejuvenation of MG wires.

In the hot-drawing process, the MG rod is thermoplastically processed in the supercooled liquid state, where the atomic structure of MGs actually undergoes a very large shear rearrangement when the diameter is changed from the millimeters to micrometers (Fig. 4). As compared to the high-temperature creep (~0.7T_g) or the cryogenic cycling method, the shear flow in thermoplastic deformation is much more homogeneous. Therefore, the shear will cause a homogeneous dilation across the whole sample and induce abundant free volume. This shear dilation will cause an increase of interatomic distance, ultimately a large decrease of elastic modulus. Meanwhile, the thermoplastic processing is conducted at a temperature just above T_g, yielding a narrow time window for thermoplastic processing. The MG wires with large specific surface area were formed in a short processing time (less than 1 s). Thus the cooling rate during the formation of MG wires is much higher. Such a high cooling rate contributes to freezing the mobile atomic rearrangement into glassy wires upon glass transition, leading to a higher energy state in MG wires (Fig. 4). The smaller the sample size, the higher the cooling rate and the severer the rearrangement of atomic structure, resulting in the size dependence of properties of MG wires. Therefore, the dramatic changes in elastic modulus of the micrometer-scale wires in this study are actually due to the combined effects of temperature, flow stress and size.

In summary, a pronounced softening has been observed in hot-drawn MG wires through nanoindentation tests. When hot-drawn into micro wires, the modulus and hardness of bulk MG rods can dramatically decrease, and decrease with size reduction. A maximum reduction of ∼26% in modulus and ∼17% in hardness is detected. The remarkable softening can be attributed to the pronounced rejuvenation which is the combined effect of thermoplastic processing and high cooling rate. Our results reveal that a proper combination of temperature, flow stress and size can change the properties of MGs significantly, thus provides a new route for tuning the internal structural state and properties of MGs. The properties of MGs may be changed after thermoplastic deformation, which may be helpful for the thermoplastic molding, especially at micro/nano-meter scales.

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