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Nano-forming of the rare earth La-based metallic glass

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ABSTRACT

Due to the unique physical and chemical properties of rare earth elements, rare earth compounds have been widely applied in many fields, such as optics, information, permanent magnet, energy, catalysis, biology and other fields. As an efficient strategy that could strongly adjust material performance, developing controllable nano-engineering method for rare earth alloys is of great significance. In the present work, we show that uniform and controllable nanowires can be readily fabricated on the surface of La-based metallic glasses. The forming mechanism was investigated and it is found that the viscous metallic glass exhibited Newtonian flow during the forming process. Owing to the unique nano-structures, the wettability could be greatly adjusted. The contact angle changed from $82 \pm 1^{\circ}$ of the smooth surface to $24 \pm 1^{\circ}$ of the structured surface. Our results throw lights on the extensive applications of rare earth nano-structures in many fields.

1. Introduction

Metallic glasses (MGs) have attracted significant attention due to their superior properties, such as high strength, excellent corrosion resistance, and soft magnetism [1-5]. One of the most desirable property of MGs could be their thermoplastic forming (TPF) ability [6]. Previous work found that MGs were metastable, when the temperature increased gradually, the intrinsic nature of MGs would change from glassy state to crystalline state [7,8]. MGs would experience a supercooled liquid region (SLR, a temperature window between glass transition temperature (T_g) and crystallization temperature (T_x)) in the process of transformation [9]. MGs show the characteristics of viscosity reducing sharply with the increase of temperature in the SLR [10]. Due to this unique characteristic, one can produce micro to nano-structures on the surface of MGs easily. Furthermore, compared with the traditional processing materials, MGs have specific advantages. MGs do not have the crystalline defects such as voids or grain boundary, meanwhile, the coefficient of thermal expansion of this material is smaller [11,12]. Therefore, the shrinkage of the formed body is quite low after processing and forming, which can ensure the size of the formed structure of MGs during TPF accuracy [13]. MGs are considered as promising micro and nano fabrication material in the future[11].

Recently, the micro and nano structures on the surface of MGs have attracted much attention because of its extended promising application in micro and nano machines, catalysts, magnetic sensors and other fields [14-17]. Previously, researchers reported the application of nano-structures of 50 nm and 20 nm on the surface of Platinum (Pt)-based MG and Palladium (Pd)-based MG in the field of nano machine and catalyst [18,19]. However, these MG systems which are noble-metal based are far from the requirements of engineering applications.. Thus, it is urgent to find a kind of MG forming nano-structures which can replace noble-metal based MGs.

Rare earth elements are very novel elements, which has been widely used in many fields. The rare earth-based MGs have also been widely studied by scientists [20-24]. Among the many rare earth-based MGs, lanthanum based metallic glasses (La-based MGs) first came into people's eyes in the late 1980s [25], La-based MGs have wide SLR, which can be easily processed by TPF, and have excellent glass forming ability [26]. Therefore, La-based MGs can replace the noble metal-based MGs to form micro and nano structures. The formation of nano-structures on the surface of La-based MGs will also give them bright prospects in many fields such as catalysis and energy. For catalysis, when the surface of La-based MGs are covered by nanowires, the active sites on its surface will also greatly increase [27,28]. In addition, the nano-structures will also change the wettability of the surface [29,30], thereby affecting the catalytic efficiency. Here we report a kind of La-based metallic glass nanowires (La-NWs) prepared on its surface by TPF, and analysis the wettability of the surface of La-NWs.

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2. Experimental Details

2.1. La-Based MG Preparation

$La_{55}Al_{25}Ni_5Cu_{10}Co_5$ metallic glass was used in present work, which was made by conventional water cooled copper mould casting in the low-pressure vacuum environment of inert gas argon, using the pure La, Al, Ni, Cu, Co metals (>99.9% purity). The prepared MG rod with a diameter of 5 mm was cut into small pieces with a thickness of 1.5 mm, and the surface of the specimen was polished with an automatic polishing machine to prevent the surface roughness from affecting the fabrication of nanowires.

2.2. Hot Pressing Details

The AAO (Anodized aluminum oxide) template with nano-scale holes was used as mold for the nano-forming in the experiment. Three types of AAO template with nano-scale holes (the pore diameter is about 330 nm, 290 nm and 170 nm respectively) were used in the experiment. The AAO template with nano-scale holes and the polished sample were mounted one on top of the other and projected into a mold with a through-hole (the diameter of 7.5 mm) in the center. After that, the sample was hot pressed in the mold under the pressure of 6 kN in the low vacuum environment at the temperature of 200-205 °C and kept pressing for 15 seconds under this condition. After that, the pressure was removed. When the sample cooled to room temperature, it was taken out of the mold and then put into an absolute ethanol solution with mass fraction of water is 0.3% to prevent the surface oxidation.

Solid NaOH particles with the purity of 97% were used to prepare a 15% wt NaOH solution. The hot pressed samples were immersed in NaOH solution for 30 minutes to clean the residual AAO template on the sample surface. After the AAO template was completely dissolved in NaOH solution, the La-based MG with nanowires on its surface was obtained.

2.3. Characterization

The amorphous nature of the samples was verified by X-ray diffraction (XRD; Rigaku MiniFlex600) with Cu Kα radiation) and differential scanning calorimetry (DSC; Perkin–Elmer DSC-8000) at a heating rate of 20 K/min. The morphology of nanowires on the surface of La-based MG was collected by field emission scanning electron microscope (SEM; FEI QUANTA FEG 450) instrument. The structure of nanowire was examined by transmission electron microscopy (TEM, JEM-2100F). DSA 100S drop shape analyser manufactured by KRUSS was used to test the wettability of sample surface. The typical volume of the used water droplet was about 2 μL. The contact angle was measured at 4-5 different positions on the surface of samples to ensure the reliability of the contact angle. In addition, both sides of the samples were tested by XRD to determine the nature of the sample.

3. Results And Discussion

3.1. Surface morphology

The whole fabrication process can be illustrated in Fig. 1(a). After constructing nanowires on the surface, La-based MG showed black luster becauseof the non-reflection of light, as presented in Fig. 1(b). The fabricated black surface of La-based MG sample with nanowires was characterized by SEM. Figure 2(a) and (c) showed the SEM image of nanowires with diameter of about 330 nm, 290 nm and 170 nm, it could be found different sizes of nano-structures cover the surface of La-based MG. High magnification SEM images (as shown in Fig. 2(d) and (f)) showed the nanowires with diameter of about 330 nm, 290 nm and 170 nm were arranged on the surface of La-based MG orderly. As shown in Fig. 2(g) and (i), the average diameters of three nanowires with different diameters were 312.8 nm, 290.6 nm and 164.3 nm, respectively.

3.2. Sample characterization

To study the nature of the La-based MG after TPF, the samples after hot pressed were characterized by XRD and DSC. Figure 3 depictedthe XRD and DSC characterization results under different diameters of nanowires. According to the XRD pattern (as shown in Fig. 3(a)), La-based MG with different size nanowires diameters showed the typical amorphous peak after TPF. It was found that under different diameter nanowires, MG can remain amorphous nature after TPF, which also provided the possibility to repeat nano-structures construction. When the nano-structures on La-based MG surface were destroyed, because samples still had the nature of amorphous alloy, the new nano-structures could be prepared on its surface by TPF again. Meanwhile, it also proved the good crystallization resistance.

The curves obtained by DSC for different samples were shown in Fig. 3(b), the glass transition temperature (T_g) and crystallization temperature (T_x) for different samples were induced in Table 1. Only small differences of thermal parameters between La-based MG with smooth surface (La-Plate) and La-NWs sample after TPF, which also proved the good forming ability and crystallization resistance of this La-based MG.

To further investigate the intrinsic structure and element distribution, the nanowire was examined by TEM observation. As shown in Fig. 4(a), a single nanowire with diameter of about 330 nm was observed by TEM, The high-resolution TEM image in Fig. 4(b) depicted that the local region of nanowire was amorphous. The selected area electron diffraction pattern of La-NW was shown in Fig. 4(c), which further showed the typical amorphous structure of La-based MG. The energy spectrum of the single nanowire was analyzed in Fig. 4(d), to distinguish the conformity between the element content of the single nanowire and the element content of the material used. We found that the element of single nanowire was lanthanum, aluminum, nickel, copper and cobalt. The elements were consistent with the elements in the materials used.

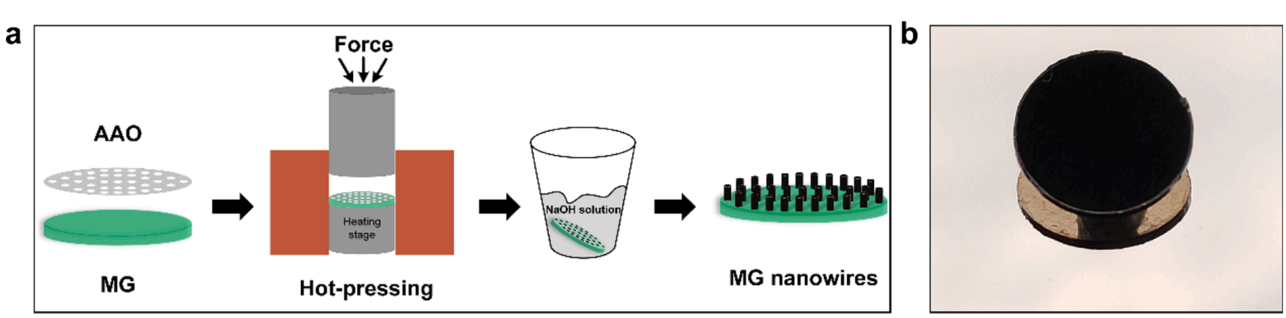

Fig. 1. (a). Thermoforming diagram of MG, (b) Surface of La-based MG with nanowires.

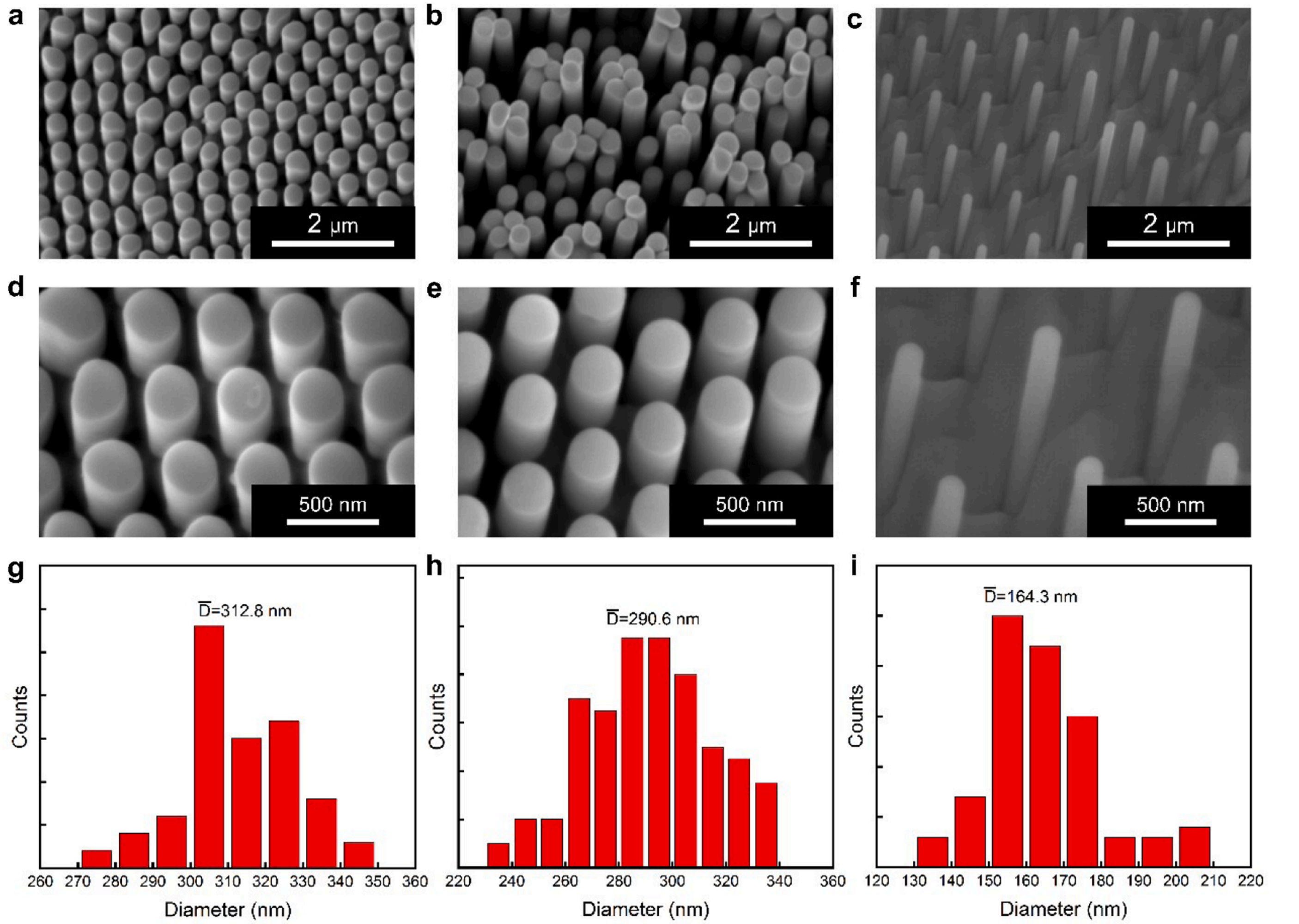

Fig. 2. (a)-(c). The SEM image of about 330 nm, 290nm, 170nm diameter nanowires at low magnification, (d)-(f) The SEM image of about 330 nm, 290 nm, 170 nm diameter nanowires at high magnification, (g)-(i) Diameter distribution of about 330 nm, 290 nm, 170 nm nanowires.

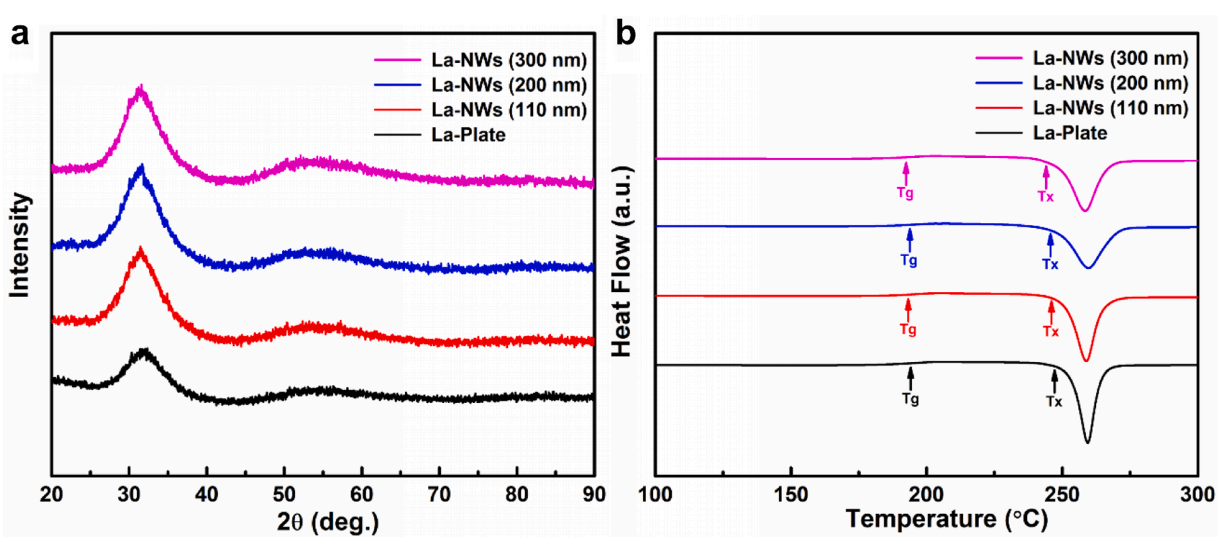

Fig. 3. (a). XRD patterns of the La-based MG after TPF, (b) DSC curves of the La-based MG after TPF

3.3. Flow behavior

It is found that La-based MG exists in the form of high viscosity in the SLR, the flow of the MG is assumed as creeping flow characteristics [31]. In addition, the formed structure is a cylinder structure, Figure 5(a) shows the hot pressed forming schematic diagram of the forming length

Table 1
Determination results of T_g and T_x in samples

Samples	T_g (°C)	T_x (°C)
La-NWs (330 nm)	191	243
La-NWs (290 nm)	190	244
La-NWs (170 nm)	189	245
La-Plate	187	246

and diameter of the cylindrical micro-structure. Hagen-Poiseuille equation can be used to quantitatively describe the required forming pressure in the SLR:

$$P = \frac{32\eta}{t}\left(\frac{l}{d}\right)^2 \tag{1}$$

Recently, it has been proposed that the pressure required for the formation of micro-structure was not only controlled by viscosity, but also the influence of capillary force should be considered when the formed structure reached the nano-scale [32]. The description of f (capillary force) can be described by following Eq. (2):

$$f = \frac{4\gamma\cos\theta}{d} \tag{2}$$

Here is the γ vacuum interface energy of metallic glass ~ $\gamma=1\ \mathrm{Nm}^{-1}$ [33], θ which is the contact angle between viscous fluid and mould.

In the process of this experiment, since the structures formed in this experiment were all at the nanometer level, we modified the above equation. The viscosity and capillary force were taken into account in the modified equation, so that the pressure needed for the micro-structure to reach the nano-scale can be described more accurately

$$P = \frac{32\eta}{t}\left(\frac{l}{d}\right)^2 - \frac{4\gamma\cos\theta}{d} \tag{3}$$

In the equation, P represents the forming pressure needed for forming different sizes of nanowires, l represents the length of nanowires, η is the viscosity of La-based MG, and d is the diameter of nanowires, t is the time required in the forming process.

Through Eq. 3, using the parameters ($P=1.36\times10^8$ Pa, $l/d\approx3$, $t=15$ s, $\theta\approx82°$, $d\approx330$ nm, $\gamma=1\ \mathrm{Nm}^{-1}$) in the experiment. The viscosity of La-based MG in TPF process was calculated to be $\eta=7.66\times10^6$ Pa s, this was basically consistent with the $\eta=7.3\times10^6$ Pa s calculated from the

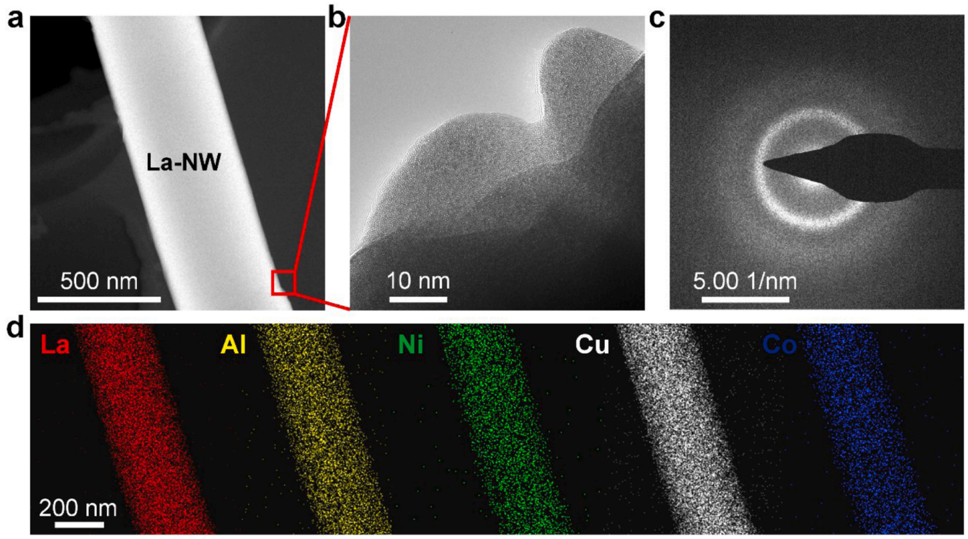

Fig. 4. (a). Morphology of a single nanowire with a diameter of about 330 nm under TEM, (b) High-resolution TEM image of nanowire, (c) Electron diffraction ring of a single nanowire with a diameter of about 330 nm under TEM, (d) Energy spectrum analysis of about 330 nm diameter nanowires under TEM.

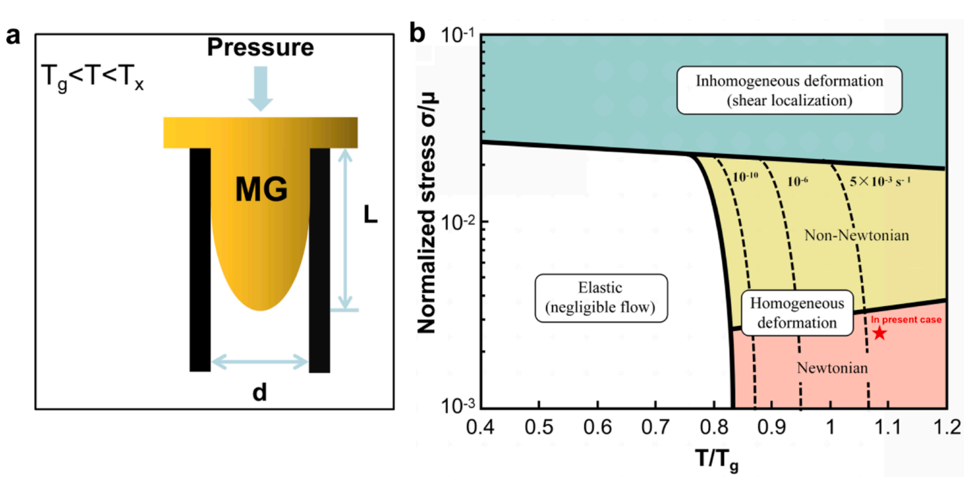

Fig. 5. (a). Schematic diagram of forming process of nanowire in AAO template at the temperature range between $T_g<T<T_x$, (b) Deformation map for MG in stress-temperature. Data in Fig. 5(b) were taken from ref. [35]. Solid red pentagram showed the case of La-based MG in TPF process.

Vogel-Fulcher-Tamman(VFT) equation [34]. That was to say, La-based MG can be quantitatively described by the above equation when the nano-structures are formed in the SLR.

The filling behavior of La-based MG in SLR was a fluid flow behavior. As shown in Fig. 5(b), to more accurately grasp the fluid flow behavior of La-based MG in the SLR, We referred to the deformation diagram of MG under stress-temperature constructed by Christopher A. Schuh [35]. The solid line in Fig. 5(b) divided the whole graph into 4 small areas, the Newton deformation, the non-Newton deformation, the elastic and the shear localization. The dashed lines in the figure represented different strain rates. The solid red pentagram showed the temperature and stress of La-based MG in the TPF process, and the area of the pentagram was a homogeneous Newton fluid region. This was in agreement with the observed compression test results.

3.4. Wettability of La-NWs

We conducted the contact angle measurements to observe the wettability of the surface when La-based MG was introduced into the nanowires with the diameter of about 330 nm. As shown in Fig. 6(a) and

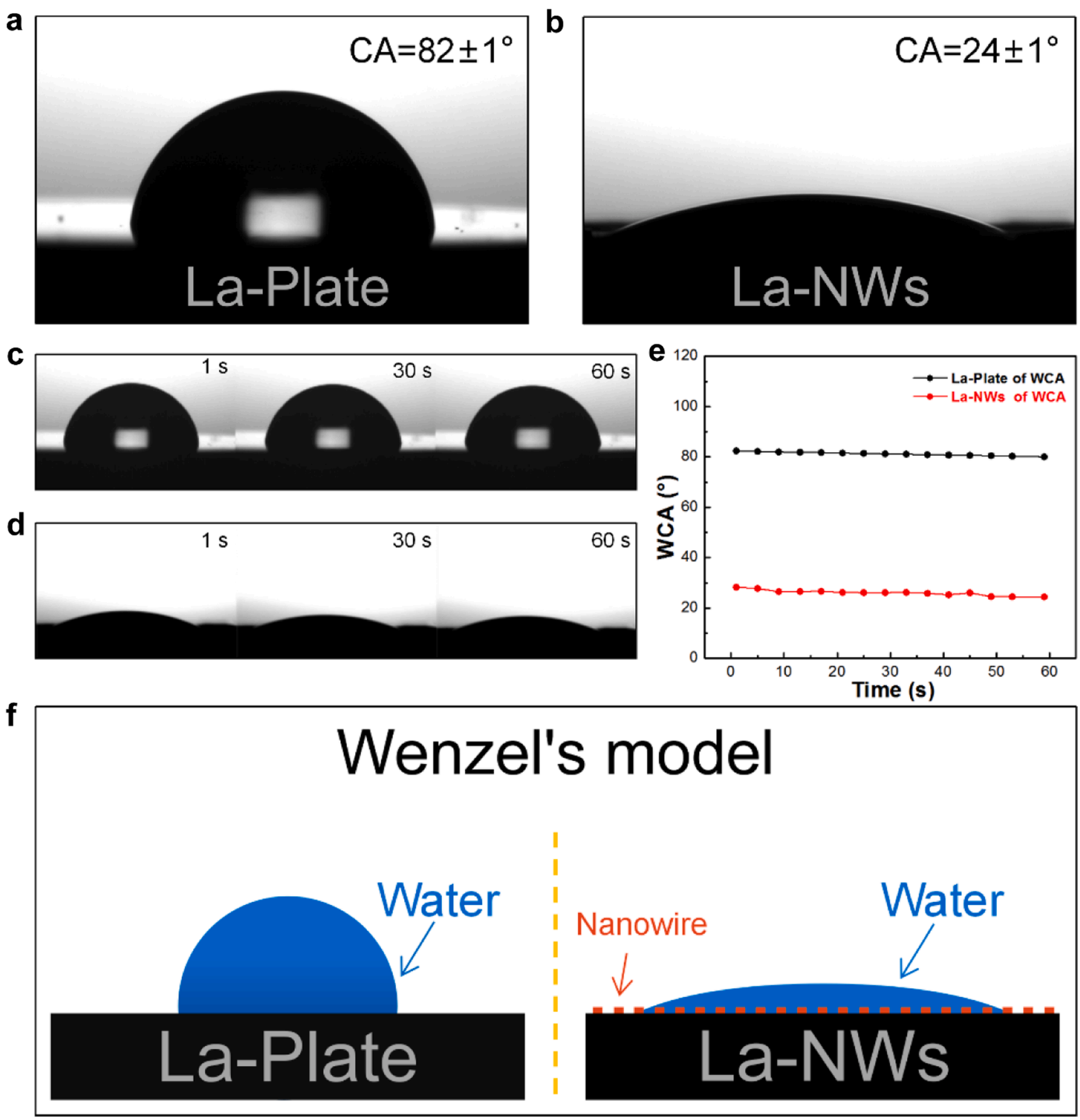

Fig. 6. (a). Water contact angle of La-Plate, (b) Water contact angle of La-NWs, (c) The change process of water droplet on the La-Plate, (d) The change process of water droplet on the La-NWs, (e) Diagram of contact angle with time, (f) Contact of water droplets on La-Plate and Contact of water droplets on La-NWs (Wenzel's mode).

(b), the contact angle of water droplets on the smooth La-Plate was 82±1°and La-NWs surface was 24 ± 1°, it showed that La-NWs had better hydrophilicity than La-Plate. Figure 6(c) and (d) showed the contact of water droplets with La-Plate and La-NWs at three different time nodes, respectively. It could be seen that the contact angle of La-Plate and La-NWs was almost stable. Figure 6(e) summarized the change of droplet contact angle with time on La-Plate and La-NWs. The chemical factors between the solid surface and the liquid and the micro and nano structures on the solid surface played an important role in the wettability of the solid surface [36]. The influence of the surface micro and nano structures on the wettability of solid surface was more significant [37]. Cassie-Baxter and Wenzel two classical models could be used to explain the influence of surface micro and nano structures on wettability. According to Cassie-Baxter model, when a water droplet contacts a surface with a geometric shape, the air was trapped in the micro-structure forming a composite interface, which prevented the liquid from wetting the solid surface [38]. Wenzel's model considered that the roughness of the surface will change when the micro and nano structures were introduced into the surface, which made the original hydrophilic surface more hydrophilic (as shown in Fig. 6(f)). [39]. In our experiment, the introduction of La-NWs has changed the roughness of the original surface. Thus, the wettability of the surface can be described by the following equation:

$$\cos\theta_w = r\cos\theta_d \tag{4}$$

Whereθ_W is the contact angle under Wenzel's model, r is the roughness coefficient, andθ_d is the contact angle on the smooth surface of the same material. According to the Wenzel's model, we can clearly see that the smooth surface with hydrophilic characteristics becomes more hydrophilic after the surface roughness changes, this is consistent with the experimental results we observed.

4. Conclusions

To sum up, nanowires with different diameters were prepared on the surface of La-based MG by TPF. In addition, the formation mechanism of La-NWs was studied, and it was found that the flow behavior of La-NWs is homogeneous Newtonian fluid deformation. When the nanowires structure were introduced into the surface of La-based MG, the contact angle changed from 82 ± 1° of the smooth surface to 24 ± 1° of the La-NWs surface, the surface became more hydrophilic. Our research results provide a new choice for people to prepare nano-structures by a top down nanomolding method. Moreover, this multifunctional surface with nano-structures will have a very broad prospect.

5. Credit authorship contribution statement

Jianan Fu: Conceptualization; Data curation; Formal analysis. **Zhiyuan Huang**: Investigation; Methodology; **Jian Yang**: Investigation; **Jiang Ma**: Supervision, Resources, Writing – original draft, Writing - review & editing. **Jun Shen**: Supervision.

Declaration of Competing Interest

We would like to submit the enclosed manuscript entitled "**Nanoforming of the rare earth La-based metallic glass**", which we wish to be considered for publication in **Journal of Non-Crystalline Solids.** No conflict of interest exits in the submission of this manuscript, and manuscript is approved by all authors for publication. I would like to declare on behalf of my co-authors that the work described was original research that has not been published previously, and not under consideration for publication elsewhere, in whole or in part. All the authors listed have approved the manuscript that is enclosed.

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