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Short communication

Surface functionalization of Zr-based metallic glass by direct nanosecond laser texturing

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ABSTRACT

The functional properties of metallic glasses (MGs) can be enhanced by introducing special micro/nano-structures on their surface. In this study, a nanosecond pulsed laser was used to texture micro-convex array structures with different pitches (*P*) on a Zr-based MG surface to enrich its engineering applications. The reflection characteristics and wettability of polished and textured surfaces were compared. The experimental results showed that unlike the bright spot reflected from the polished surface, the light reflected from the textured surface would induce a well-defined diffraction pattern. In addition, the wettability of the surfaces covered with micro-convex array structures was also different from that of the polished surface. That is, without post-processing, the textured array structures would promote hydrophilicity; while after exposing in the air for 100 days or fluoroalkylsilane modification, the textured array structures facilitated hydrophobicity.

1. Introduction

With a combination of extraordinary physical and chemical performances, metallic glasses (MGs) are recognized as promising functional materials for many research fields [1–7]. At the same time, surface functionalization by the introduction of special surface micro/nano-structures will further enrich their engineering applications [8–11]. However, drawbacks such as inherent hard-brittle feature and temperature sensibility have brought great challenges to the precision processing of MGs. In this regard, pulsed laser processing technology with merits of versatility, non-contact as well as ultra-fast heating and cooling rate [12], has been extensively utilized in surface texturing of MGs for tuning their functional properties [13–16]. For instance, by femtosecond laser processing of a Zr-based MG, Gao et al. [8] fabricated periodic gratings with various depths, accordingly displaying diverse colors. Through nanosecond pulsed laser processing, typical micro-dimple structures could be generated on a Zr-based MG surface, thereby changing its wettability [14]. Recently, we reported [17] a novel and regular micro-convex structure, which was obtained by direct nanosecond pulsed laser ablation of a typical Zr-based MG. Being similar to the periodic gratings and micro-dimple structures, surfaces with micro-convex structures may also endow MGs some promising functional properties. In consequence, this paper investigates the influence of laser-induced micro-convex array structures on the functional properties of a Zr-based MG, focusing on its reflection characteristics and surface wettability. The goal is to realize the surface functionalization of MGs, thereby accelerating their engineering applications as functional materials.

2. Materials and methods

The commercial $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ MG Vitreloy 1 (purchased from PESHING NEW METAL, China) was polished by a precision polishing machine to a mirror-like surface, with a roughness of around 10 nm. A nanosecond pulsed laser (SP-050P-A-EP-Z-F-Y, SPI Lasers, UK) was utilized to fabricate micro-convex structure on the MG surface under the protection of high purity argon with a pressure of 0.01 MPa. According to our previous research [17], the texturing parameters were

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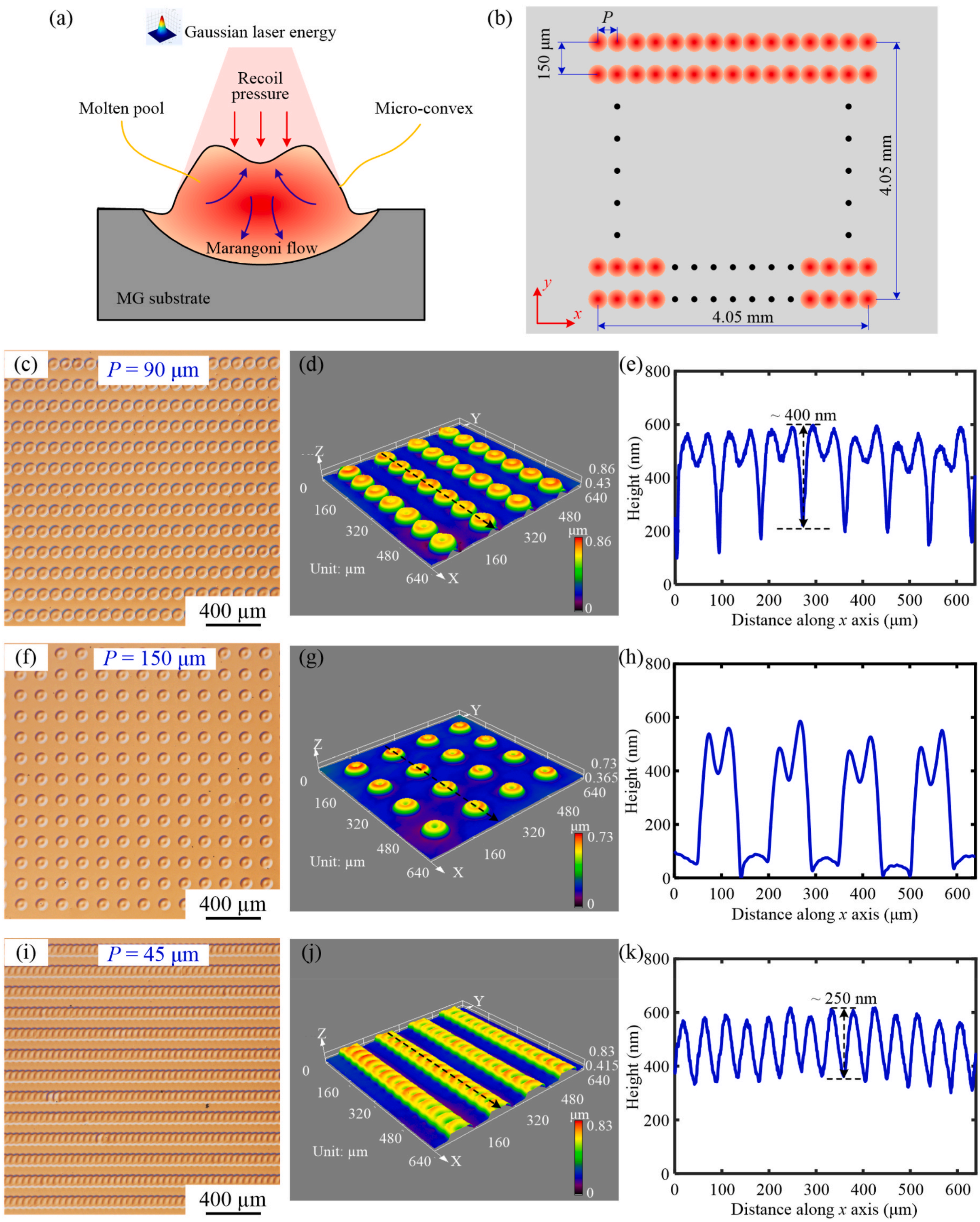

Fig. 1. Schematic diagrams of (a) the formation mechanism of micro-convex structure and (b) the designed micro-convex array structure. Optical images and 3D topographies of the textured surface under different *P*: (c) and (d) *P* = 90 μm, (f) and (g) *P* = 150 μm, (i) and (j) *P* = 45 μm. (e), (h) and (k) illustrate the cross-section profiles along the mark lines in (d), (g) and (j), respectively.

selected as follows: the laser wavelength was 1064 nm, the pulse width was 7 ns, the repetition frequency was 800 kHz, the peak laser power intensity was 7.5×10^{11} W/m^2, and the number of laser pulses was 800. After laser texturing using the above texturing parameters, regular micro-convex microstructure with diameter of 90 μm was generated on the MG surface, which could be attributed to the inward flow of the melt under the influence of Marangoni flow (as shown in Fig. 1(a)) [17]. In order to obtain micro-convex array structure, a square texturing area (side length of 4.05 mm) covered with various micro-convex structures (the distance along *y*-direction of 150 μm and the pitch along *x*-direction, *P*, ranging from 45 to 150 μm) was designed as shown in Fig. 1(b). After laser texturing, the morphologies and chemical compositions of textured surfaces were characterized utilizing the optical microscope (OM, DSX500, Olympus, Japan), laser scanning confocal microscope (LSCM, OLS4100, Olympus, Japan), scanning electron microscopy (SEM, JSM-IT500A, JEOL, Japan) combined with an energy dispersive

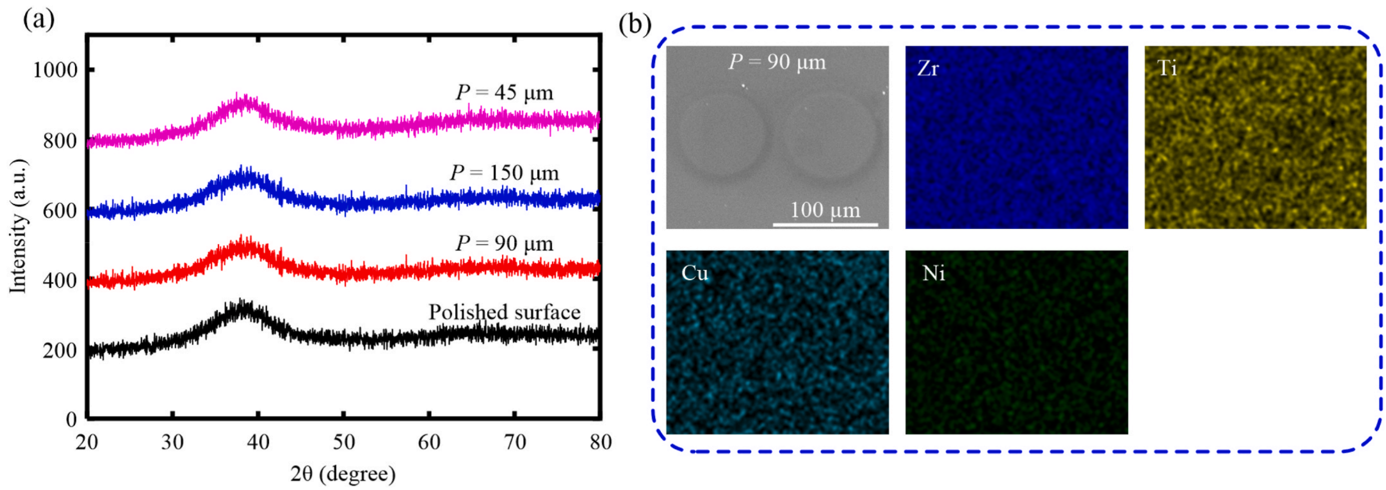

Fig. 2. (a) XRD profiles of the polished and textured surfaces. (b) SEM-EDS analyses of the textured surface under P = 90 μm.

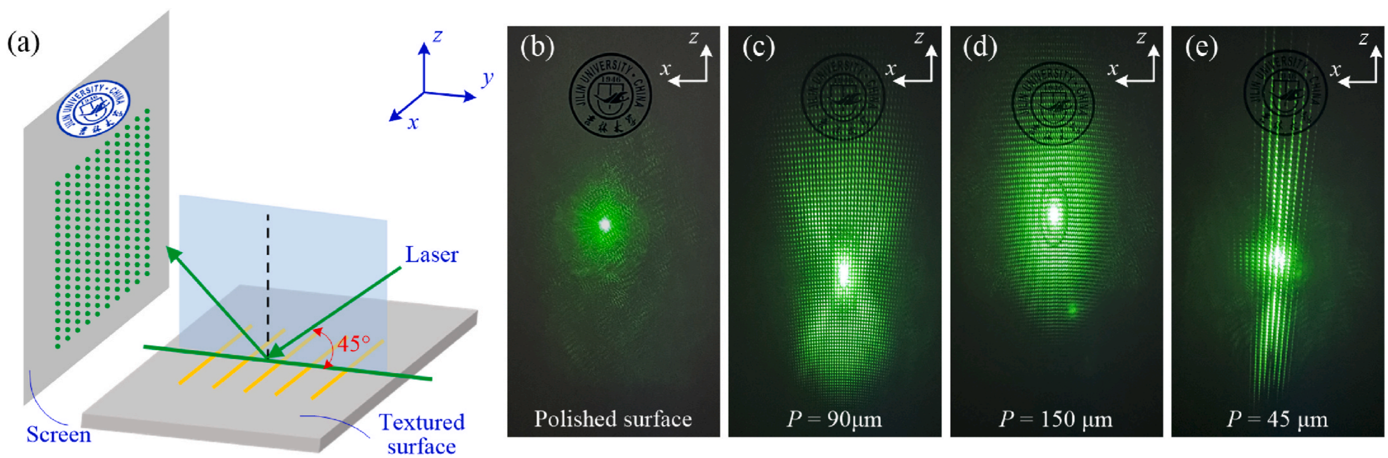

Fig. 3. (a) The schematic of reflection testing. Reflection characteristics of the surfaces under different P: (b) polished surface, (c) P = 90 μm, (d) P = 150 μm and (e) P = 45 μm.

X-ray spectrometer (EDS, EX-74600U4L2Q, JEOL, Japan), and X-ray diffraction (XRD, D8 Advance, Bruker, Germany). The water contact angles (CAs) for polished and textured surfaces were measured with an optical surface analyzer (OSA60, LAUDA Scientific, Germany). The testing liquid was deionized water with a volume of 2 μl, and three measurements were performed for each surface.

3. Results and discussions

Figs. 1(c)–(k) present the micro characteristics of textured surfaces under different P. In terms of the x direction, for P = 90 μm, the edges of the adjacent micro-convex structures are tangent, and the height difference between the highest and lowest parts is about 400 nm (see Fig. 1 (e)). For P = 150 μm, a well-defined micro-convex array structure is observed, and there are more areas between micro-convex structures that are not textured by laser. For P = 45 μm, multiple linear micro-convex structures are formed on the textured surface, and the height difference is relatively small (about 250 nm).

Since surface functions are directly affected by their surface chemistry, XRD and SEM-EDS analyses were performed on the polished and

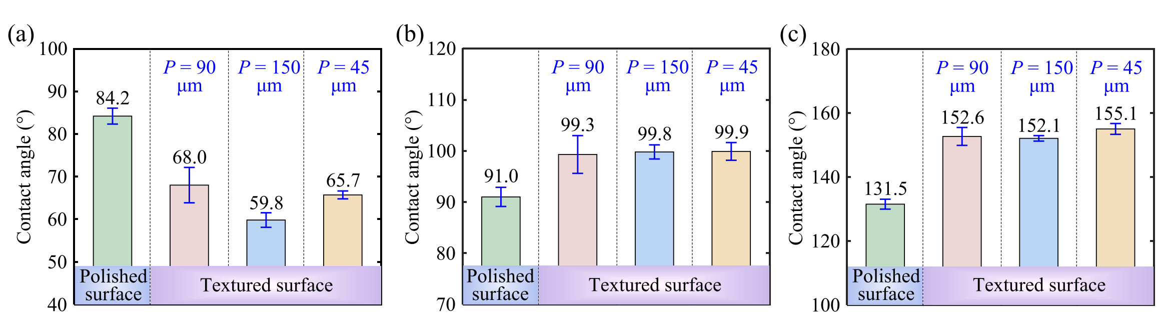

Fig. 4. The CAs of the polished and textured surfaces: (a) without post-processing, (b) after exposing in the air for 100 days, (c) after fluoroalkylsilane modification.

textured surfaces prior to subsequent functional testing to verify whether laser texturing had changed the surface chemical composition. From Fig. 2(a), for polished and all the textured surfaces, XRD profiles display broad diffraction peaks, representing the typical amorphous characteristics. Further, SEM-EDS analyses (Fig. 2(b)) show that the element distribution of the textured surface under $P = 90$ μm is homogeneous. According to the above results, it can be concluded that the laser textured surfaces are still completely amorphous and uniform in composition.

To evaluate the influence of micro-convex array structures on the reflection characteristics of MG, a simple testing method was used as depicted in Fig. 3(a). A laser pointer with a wavelength of 532 nm and a spot diameter of ~1 mm was used as the incident light source, and the incident angle was set to 45°. Figs. 3(b)–(e) present the reflection characteristics of the polished and textured surfaces. When the light falls on the polished surface, a reflected bright spot appears on the screen (see Fig. 3(b)). However, in Figs. 3(c)–(e), it is clearly seen that the reflected light from textured surfaces will induce well-defined diffraction patterns. In addition, due to the different P of the textured surfaces, the resultant diffraction patterns are also different. In particular, at a relatively small P of 45 μm, the resultant diffraction pattern is very narrow. The above experimental results well confirm the effectiveness of the textured array structures in regulating the reflection characteristics of the MG surface.

To investigate the effect of the textured array structures on the surface wettability, the CAs of the polished and textured surfaces as well as these surfaces after exposing in the air for 100 days and after fluoroalkylsilane modification were measured, and the statistical results are depicted in Figs. 4(a)-(c). As shown in Fig. 4(a), the CA of the polished surface is 84.2°, demonstrating intrinsic hydrophilicity. In contrast, the CAs of all the textured surfaces decrease to be less than 68°, which could be caused by the increased surface area [18]. After exposing in the air for 100 days, the CAs of all the textured surfaces increase to be more than 99°, which is slightly larger than that of the polished surface (91°). This may be due to a combined role of the micro-convex array structure and the organic substances it absorbs from the surrounding environment [19,20]. Similarly, after fluoroalkylsilane modification, the contact angles of all the textured surfaces are also higher than that of the polished surface. The above results demonstrate that the textured array structures affect the surface wettability: without post-processing, the textured array structures promote hydrophilicity; while after exposing in the air for 100 days or fluoroalkylsilane modification, the textured array structures facilitate hydrophobicity.

4. Conclusions

In this study, micro-convex array structures with pitch ranging from 45 to 150 μm were fabricated on a Zr-base MG without altering its chemical composition by using nanosecond pulsed laser texturing technology. The textured surfaces showed different reflection characteristics and wettability from the polished surface. The light reflected from the textured surfaces would induce well-defined diffraction patterns, instead of a reflected bright spot from the polished surface. In addition, compared with the polished surface, the textured surfaces without post-processing showed improved hydrophilicity; while after exposing in the air for 100 days or fluoroalkylsilane modification, they exhibited improved hydrophobicity. These results are expected to accelerate the engineering applications of MGs as functional materials.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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