doi:10.1246/cl.2011.191
Published on the web January 22, 2011

Spiral Pattern Formation on Bulk Metallic Glass by Electropolishing

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Spiral patterns that have concave and convex surfaces were discovered on a bulk metallic glass (BMG), $Zr_{55}Cu_{30}Al_{10}Ni_5$ atom % alloy after electropolishing under certain conditions. The observed spiral pattern had a wavelength of 2.4 µm and peaks that were 0.19 µm high. Electropolishing produces smooth metal and alloy surfaces. These patterns depend on the spatiotemporal properties during electropolishing.

Self-organization in systems far from equilibrium has attracted considerable interest in science and engineering. For example, spontaneous formation of spatiotemporal patterns such as spiral waves has been observed in living systems,[1–3] chemical systems,[4–6] and liquid crystals,[2,7] and crystals with spiral morphologies have been observed.[8,9] In electrochemistry, traveling electrochemical waves during electrodissolution,[10,11] tuning of the spacing and thickness,[12] fractal structures,[13] and spiral patterns during electrodeposition[14–17] have been reported.

Metals are electropolished to produce optically reflective surfaces by removing protrusions and defects from their surfaces. For example, electropolishing is usually used to flatten aluminum surfaces prior to anodization.[18] Yuzhakov et al. reported that the surface morphology of a dissolving aluminum anode in a commercial electropolishing electrolyte can exhibit both highly regular and randomly packed stripe and hexagonal patterns with amplitudes of about 5 nm and wavelengths of 100 nm.[19] The pattern formation mechanism during electropolishing has been investigated theoretically.[19,20] Furthermore, spirals with amplitudes less than 1 µm and wavelengths of 10 µm have been observed under certain conditions when electropolishing aluminum.[21] Spatiotemporal properties are attracting increased interest in electrochemistry.

In this letter, we report spiral patterns observed on the surface of a bulk metallic glass (BMG) plate during electropolishing. This is the first time that spiral patterns have been observed on a BMG surface. In addition, we observed spiral and target patterns on the surface of a 0.8-mm-diameter BMG rod. This implies that the pattern formation on BMGs may be independent of the surface curvature.

Figure 1 schematically depicts the experimental apparatus used. The BMG was electropolished in an electrolyte solution of perchloric acid ($HClO_4$) and glacial acetic acid (CH_3COOH). The volume ratio of $HClO_4$ to CH_3COOH was 1:15. The BMG plate consisted of $Zr_{55}Cu_{30}Al_{10}Ni_5$ atom %[22–24] and was 3 mm thick, 30 mm wide, and 60 mm high. The BMG is isotropic and homogeneous over several nanometers.[25] The top half of the BMG plate was masked with tape. The BMG plate on which the patterns were formed was connected to an anode, and two copper sheets were used as cathodes. The copper sheets were

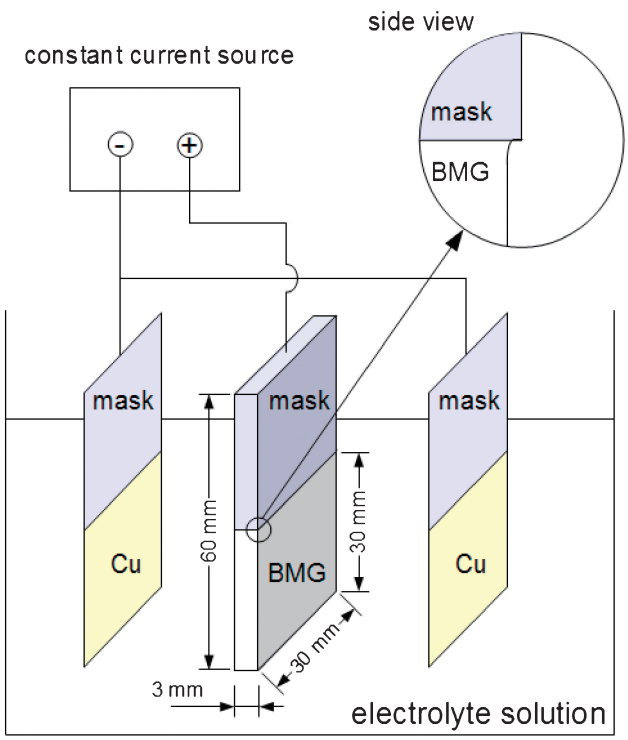

Figure 1. Schematic diagram of the apparatus used for electropolishing. The BMG plate is the anode, and the copper sheets are the cathode. The upper right corner shows a magnified illustration of an area in which patterns appear.

1 mm thick, 30 mm wide, and 60 mm high, and their top halves were masked. These electrodes were placed vertical and parallel with each other in the electrolyte solution. The distance between the plate and the sheets was about 20 mm. As the electrolysis reaction at the anode is exothermic, the electrolyte solution was cooled in an ice-water bath and maintained at a constant temperature of about 20 °C during electropolishing.

The following electrical conditions were used for electropolishing. The initial electric current of 4.0×10^{-4} A mm^{-2} was maintained for 1 min at a voltage of 37.5 ± 2.5 V. The current was then reduced to half its original value (2.0×10^{-4} A mm^{-2}) for 4 min, and these last conditions were continued for 25 min. After electropolishing under these conditions, about 30 µm had been removed from both surfaces of the BMG plate. The BMG surface was immediately washed in flowing water and then in acetone (CH_3COCH_3). We then observed the patterns on the surface with an optical microscope (Nikon, Eclipse LV150) and a laser scanning microscope (Keyence, VK8700).

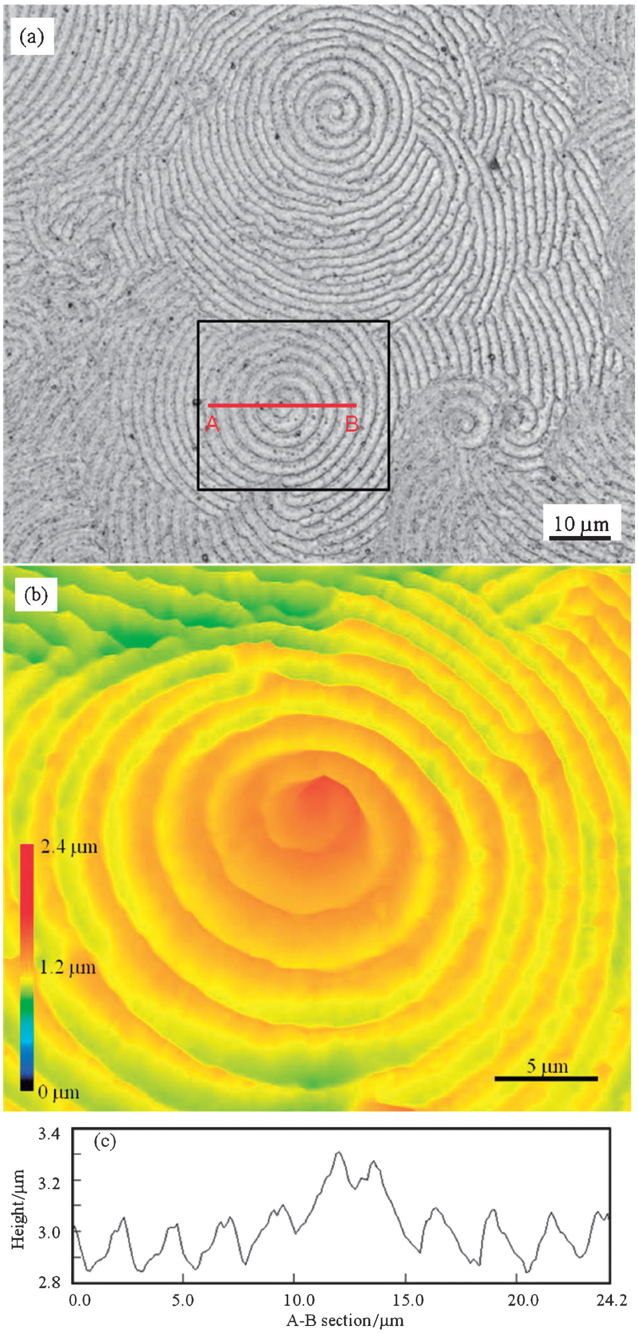

Figure 2. (a) Laser scanning microscopy image of spiral patterns on BMG surface. (b) Three-dimensional image of spiral pattern in the area indicated by the black rectangle in (a). (c) Cross-sectional profile of A–B in (a) (obtained by gradient revision using analysis software (VK Analyzer)).

Figure 2a shows a laser scanning microscopy image of spiral patterns that were observed on the BMG surface near the bottom of the masked area (Figure 1). The cores of the spiral patterns exhibit both clockwise and counterclockwise rotation. These patterns have both concave and convex surfaces. Figure 2b shows a three-dimensional image of one of the spiral patterns on the BMG surface (the rectangle in Figure 2a). Figure 2c shows the asperity along a section (line A–B in Figure 2a) of the spiral pattern on the BMG surface. These results reveal that the center of the spiral pattern is the highest point. The second and third highest points are about 0.2 and 0.25 µm lower than the center point; other peaks have similar heights to the third highest point. The wavelength and height of the peaks of the spiral pattern along the section are approximately constant being about 2.4 and 0.19 µm, respectively.

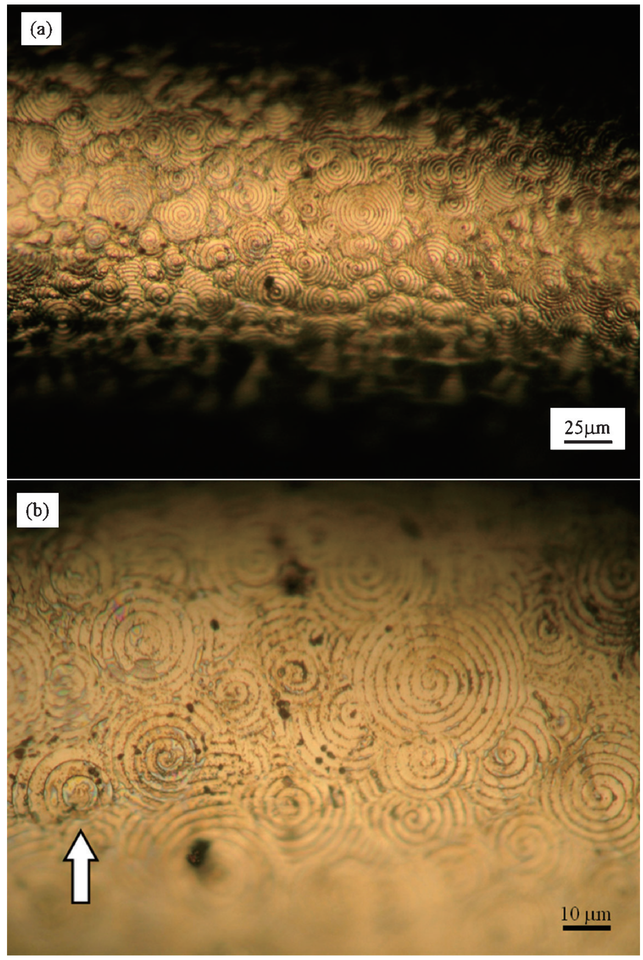

Figure 3. (a) Optical microscopy image on the BMG rod surface and (b) enlarged image.

Figure 3a shows an optical microscopy image of an electropolished surface of a BMG rod. When electropolishing the BMG rod, four copper sheets were used as cathodes to ensure a uniform current density. Figure 3a reveals that the BMG rod surface has many spiral patterns with a wavelength of about 2.4 µm. Figure 3b shows an enlarged image of the BMG rod surface. The arrow in Figure 3b indicates a target pattern.

In spite of many experimental and theoretical studies having been conducted on the surface morphologies (e.g., stripe and hexagonal patterns) of a dissolving metal anode in an electropolishing electrolyte solution, there are few reports on spiral and target patterns on a dissolving metal anode by electropolishing. In this letter, we discovered spiral and target patterns that have concave and convex surfaces on the BMG surface after electropolishing under controlled conditions. The asperity patterns appeared to be specular surfaces. The polarized surface film might be affected by gassing, which occurs during electrochemical metal removal and when the surface becomes saturated with dissolved metal. We conjecture that local dislocations of a deposited oxide might play an important role in the formation of the spiral patterns.

Finally, the observed spiral patterns qualitatively differ from growing spirals that form during electropolishing of aluminum.[21] The inside of a wave has a steeper gradient than the outside of a wave (Figure 2c). These steep and gentle slopes are similar to concentration profiles of the wave front and wave back of a propagating wave in the Belousov–Zhabotinsky reaction. The present spiral patterns may be propagating inwardly.[26] The images in Figure 3 demonstrate that they are formed on curved surfaces. There is currently no satisfactory explanation for the formation mechanism. Further experiments and numerical studies using models that consider transport mechanisms in electrochemical systems are necessary.

This work was partially supported by KAKENHI (Nos. 22740112 and 22246015).

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