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Freezing of phase separation in spatiotemporal stripe patterns formed by Ag and Sb co-electrodeposition

Yuko Nagamine *, Masahiko Hara

Local Spatio-Temporal Functions Laboratory, Frontier Research System, RIKEN (The Institute of Physical and Chemical Research), 2-1 Hirosawa, Wako, Saitama 351-0198, Japan

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Abstract

Various spatiotemporal patterns of dark and light stripes are formed in the Ag and Sb co-electrodeposition system. In this research, we investigate the time-evolution of the stripe width of a spatiotemporal stripe pattern with a size of ca. 10 μm. The results show that the stripe width increases with time and is eventually saturated. Such a phenomenon is predicted by some theories of spinodal decomposition of materials with chemical reactions in a nonequilibrium system. This suggests that the pattern is formed by the spinodal decomposition of metal alloys, Ag and Sb, with chemical reactions in a nonequilibrium system, which has not yet been reported in a metallic system.

Keywords: Silver; Antimony; Electrochemical methods; Adsorption; Self-assembly; Surface chemical reaction; Surface segregation; Alloys

1. Introduction

Spatiotemporal properties are one of the characteristics of nonequilibrium systems. Recently, materials science involving spatiotemporal properties in a nonequilibrium system [1–4], exemplified by the Belousov–Zhabotinsky (BZ) reaction [1], has attracted much attention; for example, spatiotemporal properties in the form of hydrodynamic patterns [5], defect patterns of liquid crystals [6], adsorbate patterns [7–9] and the morphological pattern of polymer blends [10] have been observed. In addition, spatiotemporal properties often exist in the biological field, for instance, neuron network patterning in the brain [11,12] or patterns on the skins of fishes or mammals [13,14]. In such biological systems, the properties of the spatiotemporal pattern contribute to the performance. Therefore, the study of materials with spatiotemporal pattern properties in a nonequilibrium system is very important in order to create artificial dynamic systems, such as analog processing utilizing the properties of spatiotemporal pattern [15].

The Ag and Sb co-electrodeposition system [16–19] also exhibits spatiotemporal properties in a nonequilibrium system, that is, in a system where Ag and Sb atoms accumulate on the electrode surface from a solution during electrodeposition. In this system, various spatiotemporal patterns are formed on the electrode surface during electrodeposition, depending on the experimental conditions, e.g., a spiral pattern, a target pattern, a spot pattern or a wave pattern, all of which consist of light and dark regions. Intriguingly, spatiotemporal patterns in this system are uniquely made of metals; in contrast, most other systems have patterns made of soft materials. The light and dark regions of the pattern in the Ag and Sb co-electrodeposition system are reported to be, respectively, rich in Ag and Sb [18]. This indicates the possibility of creating an artificial prototype with properties like those of biological systems, using metals which are suitable materials for engineering.

However, the mechanism of the formation of such patterns formed by hard materials has rarely been clarified

* Corresponding author. Tel.: +81 48 462 1111; fax: +81 48 462 4695.
E-mail addresses: n-yuko@riken.jp (Y. Nagamine), masahara@riken.jp (M. Hara).

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to date. In our previous report concerning elemental analysis [18], the phase separation of Ag and Sb in the electrodeposition system was suggested as a plausible formation mechanism for spatiotemporal patterns. Among three spatiotemporal patterns investigated in our previous research, there is a complex labyrinthine structure with a pattern size of approximately 10 μm and a movement speed of approximately 1 μm/s. As shown by our morphological measurements for the complex labyrinthine structure [19], there are grains of ca.1 μm in size that form a line on the light stripe area of the complex labyrinthine structure, following the shape of the light stripe area. Our element analysis results [18] show that the grains present on the light stripe area are mostly composed of Ag and the element composition of the grains is significantly different from those of other areas, namely, the light stripe area which extends underneath the grains and the dark stripe area. (The light and dark stripe areas are considerably richer in Sb than the grains.) We expect that grains are formed during the drying process performed in the sample preparation for morphological and elemental analyses [18,19] and that the grains may exist as a liquid layer on the light stripe area in the moving complex labyrinthine structure during Ag and Sb electrodeposition. Because the grains could not been seen by real-time observation under high magnification of an optical microscope while the complex labyrinthine structure was moving in the solution during Ag and Sb electrodeposition, as shown in Fig. 1a. Fig. 1a shows the appearance of the liquid layers covering the light stripe area. We surmise that this liquid layer, which covers the light stripe area and transforms into grains after the drying process, may be Ag-rich. That is, in the complex labyrinthine structure system, the Sb-rich dark stripe areas and Ag-rich liquid layers covering the light stripe areas are spatially separated while they have different elemental compositions. This would mean that the dark stripe areas and the liquid layer could result from the phase separation of the binary metal alloys of Ag and Sb.

Such a concentration difference is not caused by a reaction-diffusion system. In a reaction-diffusion system, distinct stripes in patterns are formed by the difference in the states of chemicals (an oxidation state and a reduction state). Except for oxygen and hydrogen, the concentrations between stripes are uniform. Although our elemental analysis results for the dark stripe areas in the complex labyrinthine structure [18] support the oxidation of Sb, only the difference in the chemical states of Sb does not create a distinction between the dark stripe areas and the liquid layers covering the light stripe areas. Our elemental analysis results [18] do show a clear difference in the concentrations of Ag and Sb between the dark stripe areas and the liquid layers. This means that phase separation of binary metals, Ag and Sb, may contribute to the separation of the dark stripe areas and the liquid layers.

However, in this electrodeposition system under examination, Ag and Sb atoms are always supplied to the electrode surface from an electrolyte solution and the mass

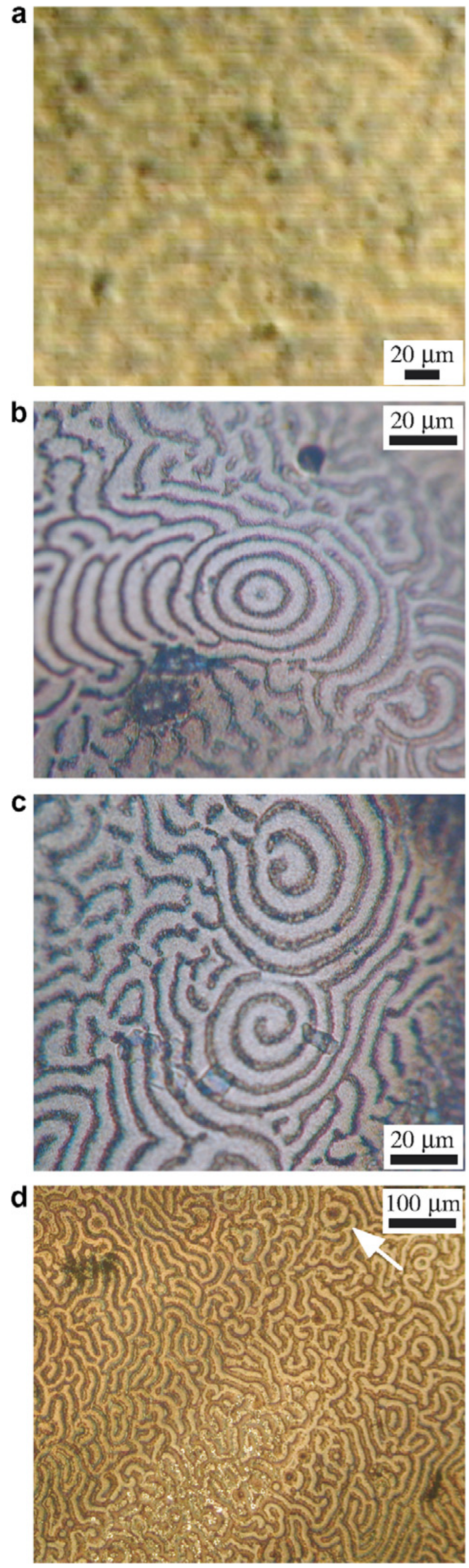

Fig. 1. (a) Optical microscope image of a complex labyrinthine structure under high magnification. (b–d) Reflection-type of differential interference microscope images of complex labyrinthine structure. (b) Image of target pattern, which exists locally in the complex labyrinthine structure, such as the region indicated by a white arrow in (d). The target pattern is a traveling wave. (c) Image of spiral patterns, which are part of the complex labyrinthine structure. This spiral pattern is also a traveling wave. (d) Image of the wide area of a complex labyrinthine structure.