Selective oxidation/crystallization and their patterning on metallic glass by laser irradiation

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Periodic lines, approximately 15-μm-wide and separated by several hundred micrometers, were prepared on the surface of Zr55Cu30Al10Ni5 metallic glass by scanning a focused laser beam across the samples in air. The X-ray diffraction (XRD) and transmission electron microscopy (TEM) suggested that the lines produced by the focused laser beam consisted of localized metal oxides (tetragonal ZrO2, monoclinic ZrO2) and crystallites (Cu10Zr7), which was in contrast to the amorphous substrate. The electron backscatter diffraction (EBSD) also confirmed the successful patterning of the lines which was mainly composed of the fine ZrO2 grains. The energy dispersive X-ray spectroscopy (EDS) mapping clearly exhibits that high amounts of zirconium (161% of the nominal composition) as well as oxygen (58.9%) and a certain amount of aluminum (80% of the nominal composition) were presented in the beam-scanned area. The Auger electron spectroscopy (AES) was also conducted to see the atomic percentage from the top surface to the depth direction and showed that the created oxides were thermally stable and therefore oxidation cannot proceed with increasing the number of laser scan. We confirmed that the laser irradiation method has a large degree of freedom for designing patterns, such as interdigital, dots, and letters because of the precise control over the scanning stage.

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1. Introduction

Recently, a lot of studies have investigated the formation of periodic patterns on the surface of substrates. Many strategies for making patterns have been proposed over the past years because they can add many new physical and chemical functions to materials, such as hydrophobic [1–3], optical [4,5], friction [6] and electromagnetic properties [7,8]. One of the most familiar and predominant techniques is lithography, which enables the fabrication of precise patterns with high reproducibility[9,10]. However, because of the high costs of the equipment (e.g. photo masks) and time-consuming nature of the technique since multiple steps are required (e.g. spin coating, exposure, removing resist, etching, etc.), alternative methods for industrial applications are desired. Super-plastic forming and imprinting is another candidate to prepare the precise patterning. Saotome et al. and Kumar et al. already reported the fabrication of some kinds of patterned materials by using the method [4,11]. However, they still have many obstacles to overcome during the processes (e.g. difficulty in preparing a precise mould with a high strength, how to release the sample from the mould after deformation is another big issue). From the background, cheaper, faster and easier patterning techniques are needed.

Meanwhile, Jordi et al. reported that nanoindentation is one of the promising techniques for the selective patterning [12]. They found that crystallites a few nanometers in size were observed in the area nanoindented in a Fe87.7B20Cr12Nb0.3 metallic glass system, suggesting that crystallization can be induced through local mechanical deformation or compressive stress without the need for thermal annealing. Then they successfully fabricated the selective patterning of nanocrystalline phases on metallic glass surfaces. They finally concluded that nanoindentation is a much less complex technique and offers an effective patterning procedure for metallic glass surfaces.

Nanoindentation as a patterning technique is interesting, but it has some drawbacks. For example, it is only able to create patterns of dots, and the production of lines or other shapes is not possible. In addition, it is not suitable for patterning large areas. Therefore, these drawbacks limit its use in practical applications.

In contrast to this method, laser irradiation is a much easier and
faster technique for fabricating patterns without the need for multiple steps, and is thought to be one of the most effective methods for patterning [6,13,14]. These advantages have led to intensive studies to find suitable materials for laser irradiation. Gao et al. reported the successful fabrication of laser-written microscale supercapacitors on hydrated graphite oxide films [15]. In addition, Xiao et al. demonstrated the selective patterning of indium tin oxide (ITO) on flexible polyethylene terephthalate (PET) substrates with a picosecond laser ablation technique [16].

While much research has been carried out on laser treatments with thermally stable materials, there have been few studies on metallic glasses. This is because there is still great concern about the formation of undesirable phases not only in the beam-scanned region, but also in the whole substrate [12].

Recently, Huang et al. reported that hierarchical micro/nanostructures was successfully fabricated on the Zr41.2Ti13.8Cu12.5Ni10Be22.5 metallic glass substrate by nanosecond pulsed laser irradiation in vacuum [17]. In their report, they showed that the laser irradiated regions as well as surrounded non-irradiated area still retained amorphous characteristic. They created the increased effective surface areas on the metallic glass without any phase changes. Fornell et al. reported that the laser irradiation of a metallic glass in air with a relatively low-power laser successfully fabricated the desired microstructure states [18]. They investigated the effects of the surface laser treatment on the structure of the Cu47.5Zr47.5Al5 metallic glass. In their study, the laser treatment was applied at a beam speed of 10 mm/s with three different laser intensities (28.5, 29, and 30 A) in an attempt to induce varying levels of surface damage on the glass. After the treatment, they found different microstructures had formed on the surface of the glass, from structurally relaxed amorphous states to oxide/crystalline states. However, the selective formation and periodic patterning of those phases has not yet been successfully achieved. Very recently, the selective surface patterning of nitride on the Zr-based metallic glass substrate was reported [19]. In the report, the patterned lines in a few mm² square area was successfully fabricated. Although the patterning seems to be attained and the hydrophobicity was surely enhanced due to a formation of a specific morphology on the surface of metallic glass by laser irradiation, there still remained some uncertainties. For instance, it was not obvious whether the patterned nitride overlapped on the amorous phase or existed separately. Since only the XRD and EDX, both of which are macroscopic observations, were used to evaluate the phase, the detail distribution of the nitride as well as amorphous phase on the substrate in the microscopic scale were still unclear. Also, the information about the created phase (e.g. the size of nitride, the percentages of the presented elements on the laser irradiated and non-irradiated area, the depth profile of each elements concentration from the top surface to interior etc.) were missing.

In this study, we designed and fabricated a selective oxide/crystalline region on the surface of Zr55Cu30Al10Ni5 glass samples with laser irradiation in air and clarified the created phase from both the macroscopic and microscopic aspects, which was the first attempt in the field of metallic glass research. One of the motivations for this study were to investigate the local phase of the irradiated/non-irradiated area and to consider whether the laser irradiation can increase the degree of freedom when designing patterned materials.

2. Experimental method

An alloy ingot with the nominal composition of Zr55Cu30Al10Ni5 (at.%) was prepared by arc melting the raw materials in an argon atmosphere. The alloy was re-melted several times to ensure homogeneity. Ribbon samples with a cross section of 0.05 × 4.3 mm were prepared with the single roller melt-spinning method. The structure of the ribbons was investigated with both XRD (Bruker AXS D8 ADVANCE) and TEM (Hitachi HF-2000). The thermal properties of the samples were examined with differential scanning calorimetry (DSC, Perkin Elmer Diamond DSC) at a heating rate of 20 K/min. Disk samples (diameter: 5 mm, height: 1 mm) were also prepared by cutting cast samples.

Lines with a length of approximately 2 mm were drawn on the surface of the samples in air (~20.6% O₂) with a fiber laser (SUMITOMO ELECTRIC SumiLas) emitted from an oscillator with a wavelength of 1060 nm. The laser oscillator itself was fixed while the stage (PI micros) holding the sample, which was placed just under the oscillator, was moved in the X, Y, and Z directions. The minimum movement step of the stage in each direction is extremely small, approximately 5.5 nm, which allows the precise patterns to be formed. The beam scanning speed (i.e., the moving speed of the stage) was approximately 0.66 mm/s, and the electric current of the laser was 0.6 A, which is much lower than that used by other researchers [18,20]. After scanning the beam, the surface of the sample was slightly polished with ion milling (GATAN PIPS model 691) in order to make its surface smooth and clean. The outer appearance of the periodic patterns was observed with scanning electron microscopy (SEM, JEOL JSM-6010LV and JEOL JSM-7100F). The morphous character of the beam-scanned sample and also only heat treated disk sample at 673 K for 1 h in air was verified with XRD. The local microstructure of the beam-scanned sample was examined with TEM (Hitachi HF-2000) and EBSD.

Fig. 1. (a) The SEM image of the laser irradiated lines and (b) their periodic patterning on the surface of the Zr55Cu30Al10Ni5 ribbon sample.

Fig. 2. The XRD patterns at the surface of the laser irradiated sample and heat treated sample at 673 K for 1 h in air.
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